XL. *Dimensional Analysis.*
By NORMAN CAMPBELL, *Sc.D.**

Summary.—A re-examination is made of the physical assumptions underlying dimensional analysis, and suggestions are offered of a method of employing dimensional arguments which is less liable to error than those at present in vogue. The final conclusion is stated in §10, the method advocated (which is not new, but the oldest method of all) in §4.

Incidentally some arguments by Jeans and Einstein, which seem to have been accepted as valid, are discussed. It is concluded that the former, while formally valid, are insignificant and do not really involve the conception of dimensions; and that the latter are completely fallacious.

§1. IN 1915 the late Lord Rayleigh wrote † :—" I have often been impressed by the scanty attention paid even by original workers in physics to the great principle of similitude." Nobody could make a similar statement to-day. During the past nine years, starting with Buckingham's work ‡, there has been a copious stream of papers, and even books, dealing generally with the principle §, while applications of it are to be found in almost every volume of every

* Communicated by the Author.
† Rayleigh (3rd Baron), ' Nature,' xcv. p. 66 (1915).
‡ E. Buckingham, Phys. Rev. iv. p. 345 (1914).
§ *E. g.* Buckingham, *loc. cit.* ; C. Runge, *Phys. Zeit.* xvii. p. 202 (1916); Ehrenfert-Afanassjewa, *Math. Ann.* lxxvii. (1916); N. R. Campbell, ' Physics: The Elements,' Camb. Univ. Press, 1920, chs. xiv., xv. ; P. W. Bridgman, 'Dimensional Analysis,' Yale Univ. Press (1922); F. London, *Phys. Zeit.* xxiii. p. 262 (1922); J. Wallot, *Zeit. f. Phys.* x. p. 329 (1922).

physical journal. Yet I do not think that Rayleigh, if he were still with us, would be entirely satisfied with the change. He would probably regret the tendency to expound the principle with great formal generality and considerable mathematical elaboration which, initiated by Buckingham, has led finally to the imposing title of "dimensional analysis"; and he would certainly regret the absurd perversions and erroneous applications of the principle which have been seriously propounded. These two things are closely associated. Rayleigh in his use of the principle was always careful to insist on the particular physical assumptions involved rather than on the general logical deduction; and it is almost certainly the obscuring of the former by an undue and entirely unnecessary elaboration of the latter that has led so many astray.

Accordingly, although I have little new to add to a discussion which is already sufficiently voluminous, it may not be waste of space to draw attention once more to the physical rather than the logical principles upon which "dimensional analysis" depends, and, reversing recent developments, to consider the manner in which it can be applied with the least elaboration and therefore with the least probability of error.

§2. Physical assumptions are introduced into dimensional arguments at three stages :—

(1) When it is decided that the systems to which the argument is to be applied are physically similar, and have throughout the same no-dimensional magnitudes.

(2) When it is decided what are the magnitudes which determine the process discussed.

(3) When definite dimensions are assigned to these magnitudes.

In most treatments of the subject, it is the second question which receives most attention : the first is often barely mentioned, and the third is answered simply by the exhibition of a list of all the principal magnitudes together with their dimensions. This last procedure I believe to be, if not actually erroneous, highly misleading ; the delusion that it is necessary for the purpose of the argument to assign to all magnitudes fixed dimensions in terms of certain fixed fundamental units is the cause of most of the difficulties that have arisen. Accordingly, we shall consider the third question first.

When we say that a magnitude has certain dimensions we mean that it is involved in some numerical law having a certain form or—to be more accurate,—if we do not mean

this, we are merely making an arbitrary statement which is
neither physically true or physically untrue, and which
cannot therefore be the basis of any physical argument *.
Now many magnitudes are involved in laws of more than one
form, and with more than one set of other magnitudes ;
accordingly, it is possible to assign to such magnitudes more
than one set of dimensions in terms of more than one set of
other magnitudes. The general practice is to select one of
the many possibilities, and to state once and for all that, in
virtue of one particular law in which the magnitude is in-
volved, it has certain dimensions in terms of certain other
magnitudes. This method of procedure can be justified † to
this extent, that it is possible by pursuing it with great care
and elaboration to found on it valid dimensional arguments ;
but it is certainly not the natural or the most convenient
procedure. The only laws that can be relevant to a con-
sideration of the behaviour of any system are the laws that
determine that behaviour ; and, consequently, the only
dimensions that are relevant are those fixed by these laws.

Surely this is obvious enough ; but if it is, how do such
questions as whether temperature has or has not the
dimensions of energy come to be debated ? ‡ The answer is
clear. The assignment of the dimensions of energy is de-
termined by the laws of a perfect gas or by theories, such as
molecular theory, which explains those laws. If these laws,
or other laws based on these theories, are relevant to the
process under consideration, temperature should be given

* I am not sure how far the truth of this statement is generally
recognized. It is, of course, implicitly involved in all discussions of the
matter that are not utterly ridiculous, but it is not often stated explicitly.
But it is difficult to see how the supposed difficulties mentioned
below could ever have arisen if it had always been borne in mind. In
case the truth of the statement is not immediately familiar, it may be
mentioned that it is discussed at great length in my ' Physics ' (*loc. cit.*).

† It cannot be justified by considering how the unit of the magnitude
would have to be changed if that of other magnitudes were changed, for
there is no compulsion whatever to change units so as to preserve the
formal constants in laws. If the inch were substituted for the centi-
metre as the unit of length, there is no compelling reason why the cubic
inch rather than the cubic foot should be taken as the unit of volume ;
indeed, since the cubic centimetre is *not* now the unit of volume, but the
volume of unit mass of water, there is no reason why the unit of volume
should be changed at all. No law can be stated in terms of choices of
units which are always, and must always remain, wholly arbitrary.

‡ The question seems first to have been put by D. Riabouchinsky in
connexion with Rayleigh's argument based on Boussinesq's equation.
Rayleigh's answer (' Nature,' xcv. p. 644 (1915)) was evasive. The
matter has been discussed by (amongst others) Bridgman, ' Dimensional
Analysis,' and Wallot (*loc. cit.*).

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the dimensions of energy ; if not, it should not. Boussinesq's equation depends neither on Boyle's and Gay-Lussac's laws, nor on molecular theory ; Rayleigh was therefore right to treat temperature as a fundamental magnitude, or rather simply as a magnitude of which the dimensions were connected in a certain manner with those of specific heat and thermal conductivity. To have given temperature the dimensions of energy would have been to introduce considerations altogether irrelevant and therefore, as Riabouchinsky pointed out, to make the problem indeterminate. On the other hand, Einstein [*], in a paper to which further reference will be made, was right to give temperature the dimensions of energy, because the assumption that the temperature is proportional to the mean energy of a molecule is inherent in his argument.

In the same manner, electric charge is to be given its electrostatic or electromagnetic dimensions according to the laws which are relevant to the problem. If charges enter only because they exert forces in accordance with Coulomb's law, then electrostatic dimensions must be used ; if they enter because a moving charge produces a magnetic field, electromagnetic dimensions should be used. If, in any problem, both electrostatic and electromagnetic forces are involved, two magnitudes must be introduced into any dimensional argument, one having one set of dimensions, the other the other.

But the removal of these difficulties is only incidental to my main purpose, which is to insist that the dimensions of the relevant magnitudes cannot be assigned, and, consequently, the dimensional argument cannot be applied, until we know exactly what are the laws determining the process that is under consideration. It is not sufficient to know what magnitudes are involved—if, indeed, it were possible to know that without knowing what laws are involved ; we must know the laws in order that the dimensions may be fitly assigned. It is true that there are certain magnitudes— liquid viscosity is one of them—which are involved in only one form of law known at present, the law namely by means of which they are defined ; but it is not permissible in all circumstances to conclude that they must have the dimensions appropriate to that law, for it is possible that other laws exist and may some day be found in which they occur. Such a conclusion is only permissible when there is strong reason to believe that it is the law by means of which they

* *Ann. d. Phys.* xxxv. p. 686 (1911).

were originally defined which is actually operative in the problem discussed.

§3. Our discussion of the third question, what dimensions are to be assigned to the magnitudes, makes the second, what magnitudes are relevant, insignificant. For of course if we know all the laws determining the process, we know the magnitudes involved in them. Let us pass then to the first, the assumption that the systems compared are physically similar.

In the simplest cases our knowledge is very direct. It is proposed to apply conclusions only to systems known to be geometrically similar, while all magnitudes other than geometrical are known to be the same throughout any one system and, consequently, necessarily similar as between two systems. This is the position in the argument applied to the simple pendulum or the acoustic resonator. The systems compared are geometrically similar, while there is for each system only one period of vibration and one value of gravity or of the velocity of sound. But few cases are so simple. Consider, for example, the familiar hydrodynamical argument, so widely used in model experiments on ships or aircraft. Here geometrical similarity is assumed, while velocity of the model and the specific properties of the medium are the same throughout any one model; but the argument will not hold unless the forces are similar—that is to say, unless the ratio of the forces acting on two parts of a model is the same for corresponding parts of all models. But there are undoubtedly many forces acting on the model. What exactly is the foundation for this assumption of the similarity of the forces?

I think it can only be found—and this is my second main conclusion—in the form of the elementary laws which determine the motion. These laws are expressed by differential equations which, in the example taken, can be written down completely. If they could be solved by straightforward analysis a complete solution could be obtained, and there would be no need of the dimensional argument at all : that argument is merely a way partially to evade insuperable mathematical difficulties or practically impossible numerical labour. Now the mathematical process of integration corresponds to the physical process of addition ; the addition of similar magnitudes belonging to two systems can only lead to magnitudes of the same kind belonging to those systems which are also similar. The argument which leads to a belief that the systems considered are similar in respect of all relevant magnitudes may therefore be stated thus. A certain

equation, involving certain magnitudes, is true of every element of each of the systems considered. (In our example the element is spatial; in others it is temporal, or, more rarely, defined by magnitudes of other kinds.) The elements of any one system are similar to corresponding elements of any other system in respect of all the magnitudes concerned in the equations ; and consequently if, by integration or the summation of magnitudes characteristic of these elements, any relation is obtained true of magnitudes characteristic of the systems as wholes, these systems must also be similar in respect of these magnitudes. There is only one point in this argument to which any doubt can attach, namely the assumption that the integration of the equations will lead to a relation between magnitudes which, being of the kinds characteristic of the elements, are also charac- teristic of the whole system. Thus, in our example, it is not certain from a mere inspection of the fundamental differential equation that there will be any resistance to the motion of the body, determined by a constant velocity ; integration might have led to the conclusion that the body would move in discontinuous jerks. Or—to take another example which may seem more plausible—it is not immedi- ately obvious from the differential equation of the motion of the pendulum that the motion will be periodic and that the system will have a period. The conclusion is only justified by experimental knowledge that there is a relation of the type sought ; it is here that assumption (2) of p. 482 enters in a way that is not an immediate consequence of assump- tions (1) and (3).

§4. The conclusion that I want to enforce is that, in some of the problems to which dimensional arguments are applicable, the argument is only valid if the laws determining the behaviour of the system are completely known, and are actually expressible in the form of differential equations, the integration of which by purely mathematical processes would give a complete solution of the problem. This conclusion is not new ; it seems to be advanced by Bridgman (*loc. cit.* p. 52), but its implications do not seem to be sufficiently recognized. For if the fundamental differential equation can be stated, all the elaboration of assigning dimensions to the magnitudes in terms of fixed fundamental units is unnecessary, and so is all the mathematical apparatus of Buckingham's Π theorem. The conclusions that it is permissible to draw follow directly from the meaning of similarity, and the identity of no-dimensional magnitudes for similar systems. Thus the fundamental hydrodynamical

differential equation for incompressible fluids is

$$\rho \frac{du}{dt} - \eta\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)u - \frac{\partial p}{\partial x} + X = 0, \text{ etc.}, \quad . \quad (1)$$

where X is a force per unit volume. Consequently, if l is a length, the following combinations must be the same for all similar systems :

$$a = \frac{\rho u l}{t p}, \quad b = \frac{\eta}{\rho} \cdot \frac{t}{l^2}, \quad c = \frac{X \cdot l}{p} \cdot \quad . \quad . \quad . \quad (2)$$

The last of these is insignificant, for p means a force per unit area; it tells us nothing that we have not already stated in introducing p. But the first two are significant. *If* there is a steady state, independent of t, and defined by (1), t must not occur explicitly; the only time that enters must be that defined by the law

$$l = u \cdot t. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Hence

$$a = \frac{\rho u^2}{p}, \quad b = \frac{\eta}{\rho u l}; \quad . \quad . \quad . \quad . \quad (4)$$

and the law required must be expressible in the form that any function $f(a, b)$ is the same for all systems. This is the usual conclusion, attained without any explicit reference to particular dimensions; all that is required is the knowledge that all terms in an equation have the same dimensions, in the simple sense that they have the same numerical values for all similar systems. The dimensional argument appears to have been originally used by Fourier in this manner.

§ 5. The question now arises whether this example is typical. I maintain that it is typical ; and that dimensional analysis, as that term is usually understood, can be validly and usefully employed only when we can write down a fundamental differential equation which (together possibly with other equations) determines the process in question, and which, if it could be integrated, would furnish a mathematically complete solution of the problem. Or since such a universal negative is difficult to prove, I would maintain more particularly that all the valid and useful applications of that analysis that have actually been made are valid and useful, only in so far as the assumptions on which the analysis is based are derived from the study of such a fundamental equation.

That statement could be justified completely only by a detailed examination of all the applications that have ever been made. Such an examination I do not propose to undertake ; for strong evidence can be brought in favour of my

contention by the examination of classes rather than of individuals. The three classes into which applications of the " dimensional analysis " naturally fall are : — I. Those in which a result is proved which had not been proved before. II. Those in which a result is proved which had been proved before. III. Those in which the result is not proved, but is assumed to be known empirically, and conclusions are advanced concerning the premises from which the empirically known result could be proved.

§ 6. I. Applications in this class are obviously useful if they are valid. All examples of it which I have discovered are valid ; and they are all of the type considered in § 4 above. In every case the fundamental differential equation was known before the application of dimensional analysis ; it was not always known to be true, and so far as its truth was uncertain the result of the application was recognized to be uncertain ; but—this is the point necessary for our purpose—the knowledge on which the use of the method here proposed could be based was available, if only in the form of an assumption. Of course, it is open to anyone to say that the knowledge was not used, and that dimensional analysis would have given the result without it ; but the facts and the arguments here advanced surely throw the *onus probandi* on those who make such an assertion. The new knowledge attained by the use of dimensional arguments was either a partial solution of the fundamental equation, which had not been solved before, or, much more often, the extension (apart from numerical constants) of a result already attained by a complete solution of the equation in the simpler cases.

And here it is relevant to notice an example in which, by the method of § 4, a correct and new result was obtained which was not obtainable (or at least was not obtained) by dimensional analysis " *. This example is the characteristic curve of a high vacuum electron current from a thermionic cathode. Langmuir † has shown that, if the electrodes are plane parallel or cylindrical concentric, the current density (σ) is connected with the voltage (V), the distance between the electrodes (l), and the mass and charge of the electron (ϵ, m) by the relation

$$\sigma = \mathrm{C} . \sqrt{\frac{\epsilon}{m}} . \frac{1}{l^2} V^{3/2}, \quad \cdots \quad \cdots \quad (6)$$

where the constant C depends on the shape of the electrodes.

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* Attention has already been drawn to this example in ' Nature,' cx. p. 10 (1922).

† Phys. Rev. ii. p. 450 (1913).

The form of this relation immediately suggests that it ought to be deducible by dimensional analysis ; but if we proceed by Buckingham's method, putting

$$[\epsilon] = [M]^{1/2}[L]^{3/2}[T]^{-1},$$

$$[\sigma] = [M]^{1/2}[L]^{-1/2}[T]^{-2},$$

$$[V] = [M]^{1/2}[L]^{1/2}[T]^{-1},$$

we can only deduce

$$\sigma = C \cdot \frac{V^2}{\sqrt{l^3 m}} f\left(\frac{e}{Vl}\right). \quad \ldots \ldots \quad (7)$$

But let us study the fundamental differential equation. It is

$$\frac{d^2 V}{dx^2} = 4\pi\rho, \quad \ldots \ldots \ldots \quad (8)$$

with

$$\sigma = \rho v, \quad \ldots \ldots \ldots \quad (9)$$

$$\tfrac{1}{2}mv^2 = eV. \quad \ldots \ldots \ldots \quad (10)$$

By elimination we get

$$\sqrt{V}\frac{d^2 V}{dx^2} = 2\sqrt{2\pi} \cdot \sigma\sqrt{\frac{m}{e}}. \quad \ldots \ldots \quad (11)$$

It follows immediately that if by integration we obtain a relation between V, the total potential between the electrodes, and l the total distance between them, measured (like x) parallel to the stream lines and to the lines of force, then it must be of the form

$$\frac{V^{3/2}}{l^2} = C \cdot \sigma\sqrt{\frac{m}{e}}, \quad \ldots \ldots \quad (12)$$

which is (6).

The reason why the dimensional argument in Buckingham's form leads to an ambiguity is that there has been omitted from it an essential assumption, namely that the stream-lines and lines of force are identical. This assumption can be introduced ('Nature,' *loc. cit.*) by treating area (or volume) as a fundamental magnitude, in place of as a derived magnitude with dimensions L^2 (or L^3). But my contention is not that, given the right assumptions, formal "dimensional analysis" will not give the right result, but that it is impossible to be sure of making the right assumptions without examining the complete equations. In this instance it is impossible without examining the equations to realise that there are two lengths involved, parallel and perpendicular

to the stream-lines, and that, while similarity in respect of the former is required, similarity in respect of the latter is not.

§ 7. II. The purpose of applications in this class is often purely didactic ; the examples are merely given to show how the argument might be applied in examples of class I. If given for that purpose, they are wholly unobjectionable, but for the original investigator, skilled in the tools of his trade, they are hardly useful. However, some writers, in giving such examples, appear to proceed beyond mere demonstration by example : they seem to imply that the fact that their methods lead to correct results shows that those methods are sound. Such an implication is, of course, objectionable in the highest degree; it is easy enough to prove a true conclusion (even from true premisses) by an unsound argument, when the true conclusion is already known. The true result proves nothing about the validity of the reasoning ; that validity cannot be established by induction, but only by a thorough examination in the light of logical principles. Moreover, even if any evidence of the validity of certain methods were established by such methods, a highly dubitable assumption remains. It is one thing to choose the magnitudes on which a process depends and to assign to them the right dimensions, when the conclusion and an argument by which it can be deduced validly are already known; it is quite another thing, when the conclusion and the argument are not known. The exhibition of these trivial examples to show how easy is dimensional analysis, without a full discussion of the assumptions involved and the nature of the argument, is the cause of all the errors to which it has given rise ; it cannot be too strongly deprecated.

Most of the previous proofs of examples in class II. depend on differential equations, and therefore could not in any circumstance offer evidence against the position here maintained. But there is one curious example to the contrary, the only one of the kind that I have discovered, which therefore needs a moment's attention.

It is Jeans' deduction [*], quoted by Rayleigh (*loc. cit.*), of the proposition that, if the viscosity of a gas varies as T^n, the force between its molecules must vary as r^{-s}, where

$$s = \frac{2}{n - \frac{1}{2}} + 1. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The complete proof of this proposition, previously given by

[*] J. H. Jeans, ' Dynamical Theory of Gases,' Camb. Univ. Press, 1904, p. 275.

Jeans (*loc. cit.* p. 256), is not derived from a differential equation. True; but there is also no application of the principle of similarity. The essence of such analysis is the deduction of a relation between magnitudes A, B, C, . . . from a relation between magnitudes *a, b, c,* A being of the same kind as *a*, but not being actually the same magnitude. If A and *a* are the very same magnitude, there is no question of similarity, which is the basis of " dimensional analysis," and which renders necessary a knowledge of the differential equation ; there is identity. Now in this case of viscosity the equations from which we start, and which take the place of differential equations, involve the very same magnitudes as those between which the final conclusion is stated. The κ, m, C, μ involved in equations (582), (583), (584) (*loc. cit.*) are precisely the same magnitudes as those introduced in the " dimensional argument" on p. 275. The result given follows by the merest algebraic elimination ; the mathematical apparatus necessary to obtain the result directly is an exact reproduction step by step of that involved in the " dimensional " argument. Dimensions are utterly irrelevant ; given the equations, the result follows whatever the physical nature of the quantities involved in them.

§ 8. III. At first sight this class might appear to provide examples of the well-known procedure whereby, from the concordance between a known empirical law and a proposed theory, we prove the truth of the theory. And this view would be correct, if the premisses from which the empirical law is deduced were some definite theory. There are cases in which this condition seems to be fulfilled ; and in all of them the theory is expressible in the form of a differential equation ; it is shown that a partial solution of that equation by the method of § 4 leads to the empirical law. Such a procedure is perfectly correct ; but in practice examples of this nature are not easy to distinguish from those of Class I. ; the distinction depends upon whether the empirical law (which is not always quite certain) or the proposed theory is regarded as the more firmly established. But these are not the typical examples of Class III. In the typical examples, the premisses are not a definite theory, expressed in any kind of equation, but the mere assumption that the process considered depends wholly on magnitudes of the kind occurring in the empirical law. (See examples below.) Now this assumption is always highly precarious, for it is liable to be false if there is involved in the process any unknown universal constant ; and laws such as these, of which, *ex hypothesi*, no theory is certainly established, are

just those most likely to involve such a constant. A simple example will make this matter clear. If we were ignorant of gravitation, we might argue that the period of a planet was to be explicable on some theory involving only a time and a length; for empirically the period depends on nothing but the radius. It is only when we recognize the universal constant of gravitation that we realize that an adequate theory must involve mass.

Further, it is not clear what such an argument could prove, even if it were valid; apparently it is suggested that an empirical law is confirmed if it can be shown to be a consequence of *every* reasonable theory. But we need not discuss this matter further; for actually all examples of this nature that I have found involve other fallacies, and since these fallacies bear out well my contention, two of them may be examined more closely.

§ 9. These examples are provided by the attempts of Einstein * and his imitators † to deduce relations between the specific properties of metals, such as the thermal conductivity, the melting-point, specific heat, and compressibility. In the paper mentioned Einstein gives three such deductions. The first is perfectly correct, and founded, like all correct deductions of this kind, on a differential equation in an earlier paper ‡. If the argument here proves anything, it is that the same result would follow from regular arrangements of the atoms (similar in all substances) other than that assumed in the detailed calculation §. The second is either valueless, reducing to a variant of the Jeans example, or incorrect. The assumption made is that the natural frequency of the material depends only on the mass and distance apart of the atoms and on their mean energy at the melting-point (or other "corresponding state"), which is measured by the temperature. Now either (1) the natural frequency

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* A. Einstein, *Ann. d. Phys.* xxxv. p. 686 (1911). I omit here all reference to Einstein's views about the numerical value of the "undetermined constant"; those have been dealt with elsewhere (‘Physics,’ pp. 427-429) —any objections which may be urged against them are independent of and additional to those with which we are here concerned.

† *E. g.*, L. Schiller, *Zeit. f. Phys.* v. p. 159 (1921).

‡ A. Einstein, *Ann. d. Phys.* xxxiv. p. 170 (1911).

§ It may be pointed out that, since the deduction is valid only if all metals are geometrically similar in the arrangement of their atoms, and since it is known now that they are not so similar, the dimensional argument shows that the formula deduced can be at best an approximation.

is the reciprocal of the time in which an atom, moving with the velocity corresponding to its mean kinetic energy, traverses the distance between two atoms, or (2) it is not. If (1), then the meaning of the quantities involved leads to algebraic equations between the very quantities with which the conclusion is concerned, the conclusion being reached by mere substitution and elimination ; no assumption concerning similarity is made, and, on the other hand, nothing whatever is added by dimensional analysis to what may be proved by the most elementary mathematics. If (2), it must be assumed that, in all metals, all frequencies are similar to this frequency : there must be no forces producing velocities which are not similar to the velocities of thermal motion. This assumption is almost certainly incorrect. A false assumption concerning similarity has been made, because a fundamental differential equation was not present as a guide.

The third example relates thermal conductivity to mass and distance apart of the atoms, natural frequency, and temperature. Now Einstein has just proved that the experimentally known relation between thermal conductivity and temperature is inconsistent with classical mechanics. The only alternative known to classical mechanics is quantum mechanics (relativity is here irrelevant). On what grounds then can he be so certain that h is not to be included among the quantities on which the thermal conductivity depends ? Yet if it is to be included, his conclusion does not follow. But there is an even more surprising assumption involved in his argument. The thermal conductivity means the energy transferred in unit time across unit area perpendicular to unit temperature gradient ; on the other hand, temperature is taken to be proportional to the mean energy of a molecule. Energy therefore enters twice ; the argument is not valid unless the two energies are similar—that is to say, it is not valid, unless in all substances under all conditions the energy flowing in times inversely proportional to the natural frequency is proportional to the mean energy of a molecule. But this condition can be attained only if a specified temperature gradient is maintained in each material at each mean temperature. Or the same objection may be put in another way which is closely connected with our observations on p. 484. In the process considered there are two laws involved, both involving temperature. One is the law of thermal conductivity, defining that magnitude, that the heat flow is proportional to the temperature gradient. The second is that the mean energy of a molecule is proportional to the

temperature. Since temperature is involved in two independent laws, it requires to be introduced twice, with two different dimensions, into the argument. Or, once again — these objections though differing in form all are equivalent,—an examination of the previous calculation shows that the fallacy enters because the atomic specific heat is taken as no-dimensional. It is so taken because it is (approximately) a universal constant. But, as has been insisted already, universal constants are not necessarily no-dimensional. Such are the fallacies into which even the greatest physicists may fall when they attempt to base dimensional arguments on anything but a complete and exhaustive statement of the laws determining the process they study.

§ 10. Our final conclusion then is this. Dimensional analysis is useful and valid only when the assumptions concerning the magnitudes involved and their dimensions are based on the inspection of equations expressing fully the numerical laws or theories by which the process under discussion is determined. If they are so based, then all the formalities which various writers have elaborated are useless; no fixed dimensions or fixed fundamental magnitudes need be introduced; all that is required is a sound appreciation of the meaning of similarity and a knowledge of the rule, which is one of its obvious consequences, that all terms in a numerical law have the same dimensions.

It is probable that, in all useful and valid cases, the fundamental numerical laws or theories are expressible in differential equations; and that the only significant result of dimensional analysis is the generalization, for cases in which those equations are mathematically intractable, of a result which can be established by full mathematical reasoning in simpler cases. It is possible that there are exceptions to this statement, though none have been discovered. In any case the errors that arise when dimensional arguments are based on anything but differential equations are so facile and so plausible that any argument not so based should be accepted only after the most careful scrutiny in the light, not of an elaborate statement of the formal logical process employed, but of the physical significance of the assumptions made.

XLI. *Viscosities of Liquids experimentally correlated to Pendulum Dampings.* By Prof. E. H. BARTON, *F.R.S.*, *and* H. M. BROWNING, *M.Sc.*, *Ph.D.*, *University College, Nottingham* *.

[Plate I.]

THE appearance of some of the exponentially-damped vibration traces obtained in the course of recent work † suggested the idea of producing such dampings by utilizing the viscosities of liquids. This seemed likely to give a simple illustration of the relations holding between viscosity and damping and possibly provide a method for the comparison of viscosities, if not for their actual determination.

For this purpose the pendulum in use carried (by brackets on its rod) a pair of planes dipping into the liquids whose viscosities were under test, and moving parallel to and at measured distances from the inner side of the vessel containing them. For the liquids, samples of glycerine were used with different water contents, their densities and temperatures being noted and therefore their viscosities calculable. On plotting graphs of the results these seemed to be consistent enough to justify the use of interpolation or extrapolation. By the latter the viscosity of a sample of oil was determined. The method therefore seems suitable for laboratory use and may perhaps be as accurate and more expeditious than some others. The apparatus could be modified so as to be suitable for viscosities as low as those of water.

Apparatus.—The photographic reproduction (Pl. I.) shows the apparatus used. One of the brackets and the dipping plates carried by it are seen towards the top of the lath and near the axis of suspension, because the corresponding tank was removed to show it. The other tank was left in position. The two tanks containing the liquids are adjustable to and from the lath so as to set by a pair of gauges the exact distance required between the moving plates dipping in the liquid and the fixed side of the tank near which they move.

The apparatus as shown is suitable for liquids like glycerine and oil, the viscosities of which range from 8 to 2 c.g.s. units. For much smaller viscosities, as that of water of the order 0·01 c.g.s. unit, the pendulum bob would be made lighter, the dipping plates larger and placed much lower on the lath. In this way the sensitiveness might be increased a hundred fold or more as desired. The board near the base

* Communicated by the Authors.
† Phil. Mag. vol. xlvi. pp. 399–406, Sept. 1923.

of the apparatus is drawn along by hand, timed by a metronome, and receives the traces of salt left by the pendulum.

Theory.—Let a lath and bob pendulum carry plane plates dipping into the viscous liquid at distance z from the plane sides of the tanks which contain it. Then we may write as the equation of motion for small oscillations

$$I\frac{d^2\theta}{dt^2} + C\frac{\eta}{z}\frac{d\theta}{dt} + G\theta = 0, \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

where I is the moment of inertia of the pendulum about its axis of suspension, C and G are constants for the pendulum, and η is the viscosity of the liquid, that of the air being neglected,

or

$$\frac{d^2\theta}{dt^2} + 2k\frac{d\theta}{dt} + p^2\theta = 0 \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

where

$$k = (C\eta/2Iz) + p\lambda_0/\pi \quad \text{and} \quad p^2 = G/I . \quad \cdot \quad (3)$$

and λ_0 is the logarithmic decrement of the pendulum due to air only without any viscous liquids in use.

The solution may be written

$$\theta = e^{-kt}(A\cos qt + B\sin qt) \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

where $q^2 = p^2 - k^2 = p^2$ nearly . . . . (5)

and A and B are arbitrary constants depending on the initial conditions.

Hence the logarithmic decrement per half-period is given approximately by

$$\lambda = k\pi/p = \{C\eta\pi/2z\sqrt{(GI)}\} + \lambda_0 \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

or

$$\lambda - \lambda_0 \propto \eta/z . . \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

Further, if the amplitude of the vibration is reduced to a half in n half-periods, we have

$$e^{-nk\pi/p} = \tfrac{1}{2} = e^{-n\lambda} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (8)$$

Thus for any given vibration, we have

$$\lambda = \frac{1}{n}\log_e 2 = \frac{0\cdot69315}{n} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (9)$$

and n will be a useful experimental gauge for λ.

Experiments.—As the viscosity of the glycerine varies so

much with temperature and with its water content (which is spontaneously varying), it was necessary to take the density before and after a set of experiments and the temperature from time to time while the experiments proceeded. The dipping plates were then successively adjusted at definite distances from the sides of the tanks by the introduction of suitable gauges of metal or wood. For each such distance a vibration trace was obtained.

Results.—The chief results of the experiments are given in the photographic reproductions in figures 1–24 (Pl. I.), the details applicable to each trace being shown in the accompanying table. The experiments with oil were really carried out before those with the glycerine, for which it proved convenient to adopt other gauges for the thickness of viscous material in use. Hence the double value for oil at the foot of the table, viz., actual observations and deductions for the same thicknesses as adopted for glycerine.

Of the 24 figures on the plate those constituting any one line are obtained from the same liquid. Those in any one column (except the bottom row figs. 21–24 for oil) are obtained by use of layers of the same thickness of viscous liquid.

The significance of the results in this table becomes apparent when graphs are plotted to exhibit the relations involved. Thus in fig. 1, the abscissæ represent the thickness z of the viscous substance and the ordinates represent the logarithmic decrement, being equal to $\log_e 2$ divided by n, the number of half-periods required to halve the amplitude of the vibration. Thus there is a separate graph for each liquid, its position in the diagram depending on the value of the viscosity concerned. Again, in fig. 2 the ordinates are as before, but the abscissæ now give the values of the viscosities, inserted for the glycerine and water from tables in Archbutt and Deeley's 'Lubrication and Lubricants' (pp. 161–164, 1912, 3rd Edition), and corrected for temperature. In this diagram a separate curve appears for each different thickness of the viscous layers. The logarithmic decrement $\lambda_0 = 0.004$ of the pendulum without any liquids in use is shown on the axis of ordinates in fig. 2. It is the excesses of the other logarithmic decrements over this $(\lambda - \lambda_0)$, which really measures the effects of the viscosities of the liquids. But this makes no difference to the determination of the viscosity. It may be seen that the other curves approximately converge to this point.

TABLE CORRELATING VISCOSITIES AND DAMPINGS.

Liquid	Densities reduced to 20° C.	Viscosities at 20° C.	Actual Temperatures of use.	Mean Viscosities at temp. of use.	Number n of half periods to halve the amplitude. Thickness of Viscous Layer.				Values $\frac{\log_e 2}{n} = \log.$ dec. $\lambda.$ Thickness of Viscous Layer.			
					mm. 0·62	mm. 0·92	mm. 1·62	mm. 5·0	mm. 0·62	mm. 0·92	mm. 1·62	mm. 5·0
	gm./c.c.	c.g.s.	°C.	c.g.s.								
< Glycerine and Water >	1·2518	6·00	16°·6 to 17°·2	7·9	8·0 *(1)	11·0 (2)	12·0 (3)	20·5 (4)	0·0866	0·0623	0·0577	0·0338
	1·2466	4·10	17°·4	5·11	9·0 (5)	11·7 (6)	18·7 (7)	30·5 (8)	0·0769	0·0593	0·0371	0·0227
	1·2430	3·30	16°·2 to 17°	4·5	11·7 (9)	17·0 (10)	22·0 (11)	35·5 (12)	0·0593	0·0407	0·0315	0·0195
	1·24115	2·90	17°·8 to 18°·4	3·48	15·7 (13)	23·3 (14)	30·0 (15)	47·0 (16)	0·0433	0·0298	0·0229	0·0148
	1·23225	1·82	14°·5 to 16°·5	2·73	22·3 (17)	24·0 (18)	34·5 (19)	58·0 (20)	0·0311	0·0289	0·0207	0·0119
			Deduced Values for Oil >						0·028	0·0214	0·0145	0·00866

log. dec. $\lambda_0 = 0·004.$

Actual Thicknesses of Viscous Layer of Oil.

					mm. 0·3	mm. 0·7	mm. 1·4	mm. 5·2	mm. 0·3	mm. 0·7	mm. 1·4	mm. 5·2
< Oil >				2	9·5 (21)	27 (22)	42·5 (23)	80 (24)	0·073	0·0256	0·0163	0·00866

Without any liquid

log. dec. $\lambda_0 = 0·004.$

Fig. 1.

Fig. 2.

2 K 2

From the curve plotted for oil on fig. 1, we obtain the ordinates corresponding to the thicknesses used in the experiments on glycerine. And these are inserted in the table and plotted for oil in fig. 2. Thus the viscosity of the oil is determined to be 2 c.g.s. units, by extrapolation from the values for glycerine.

Nottingham,
    December 11th, 1923.

XLII. *Experiments on the Artificial Disintegration of Atoms.*
   *By* Dr. GERHARD KIRSCH, *Vienna, and* Dr. HANS PET-
    TERSSON, *Gothenburg* [*].

IN the course of a still unfinished series of attempts to accelerate the radioactive disintegration Uranium I—Uranium X through intense bombardment with α-particles, one of us has found a new method for obtaining strong preparations of radium C from radium emanation [†]. With the simplest type of apparatus used for this purpose, a vertical cylinder of best Invar steel, ground conical at its upper end so as to fit into the neck of a small quartz recipient containing dry radium emanation, has its lower end kept immersed in liquid air. The upper end of the cylinder is covered with a thin foil of the metal to be activized, or else it carries a thin disk of the same material screwed into the steel. The emanation rapidly freezes out on the cooled surface, where it is kept in frozen condition for a couple of hours, so as to leave sufficient time for the active deposit to accumulate. The steel is then heated to room temperature while the emanation is pumped off, the activized metal is purified from emanation by the ordinary method and its γ-activity is measured. The yield of radium C, which is generally between 40 and 50 per cent., may be considerably increased, in fact nearly doubled, by covering the frozen emanation as soon as it has settled on the metal with a piece of very thin metal

[*] Communicated by the Authors.
[†] H. Pettersson, *Mit. Inst. f. Radiumforschung*, Nr. 155, *Wiener Ber.* Bd. 132, p. 55 (1923). Owing to other work intervening, the experiments to be described in this paper, which were started in April 1922, have had to be discontinued twice. As they will now again be interrupted for at least several months, we have decided to publish a brief report on the results hitherto gained, although they are mainly methodical in character.
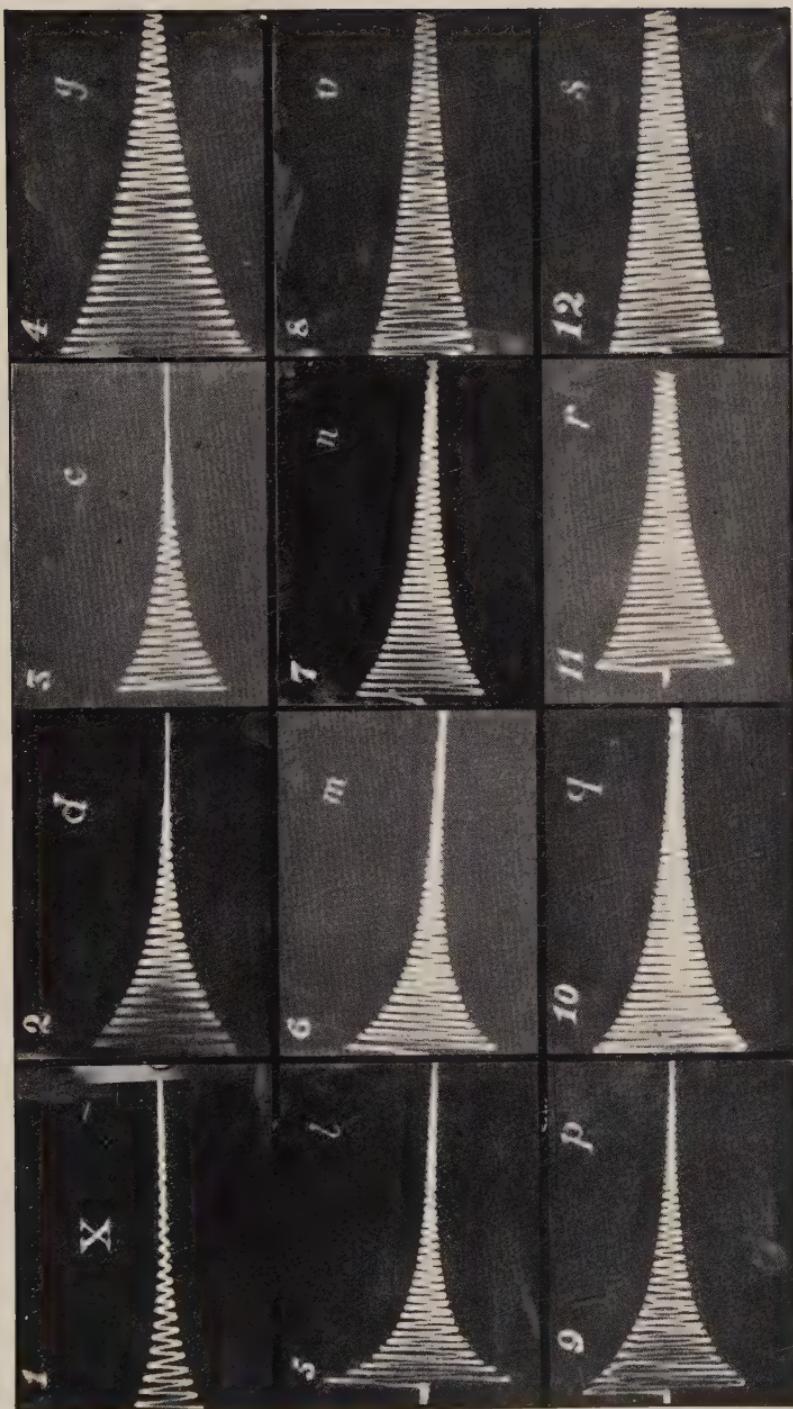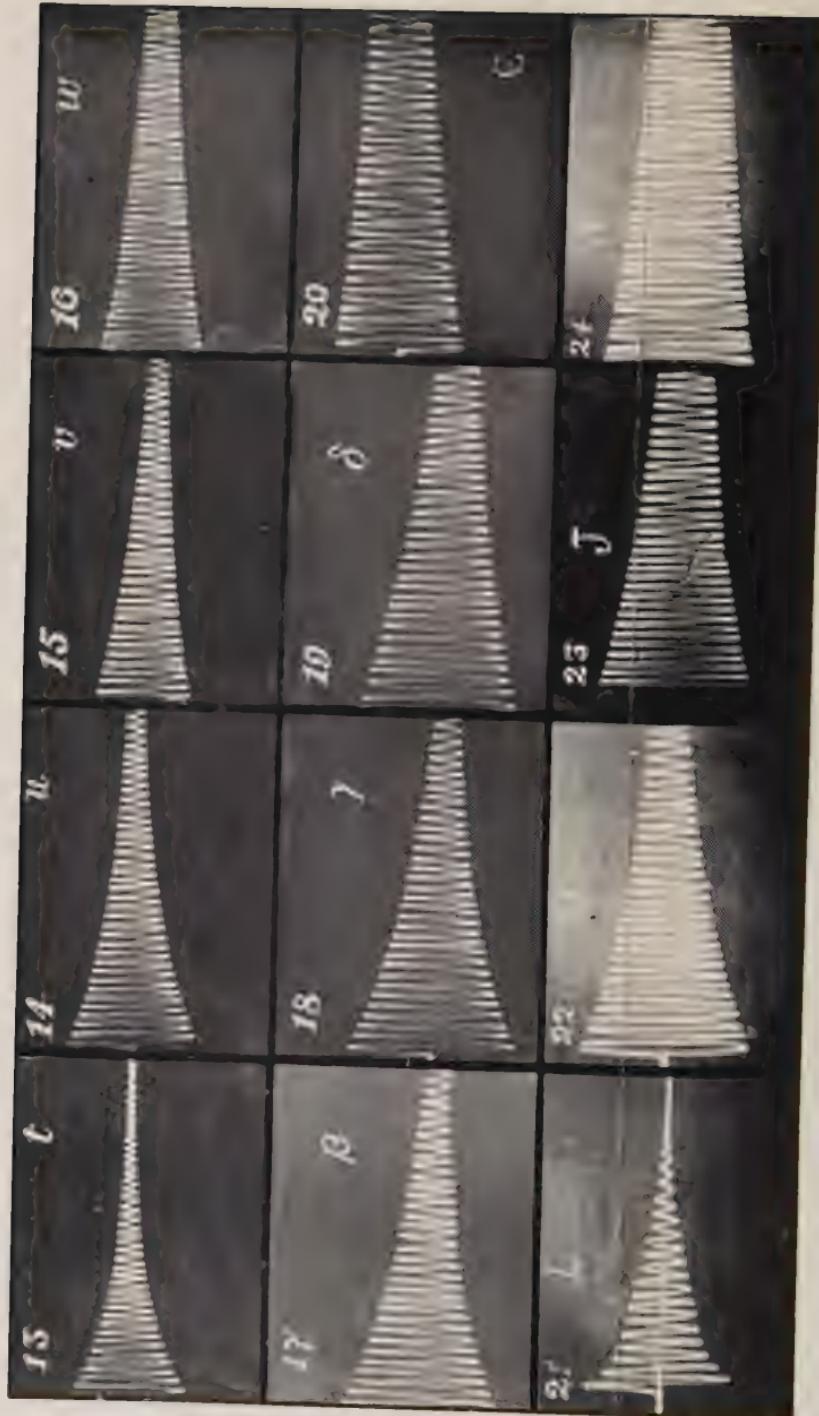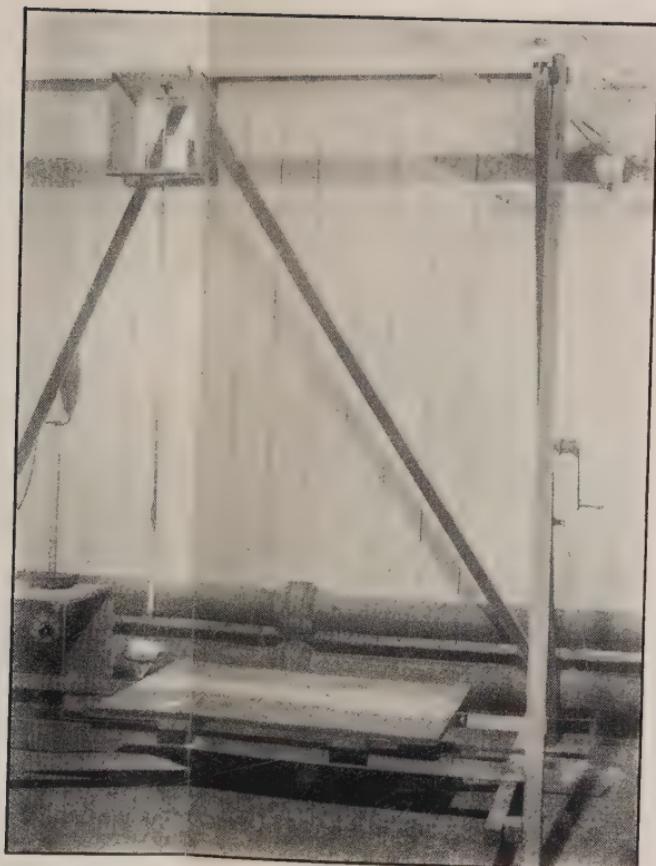
Photograph of Apparatus.

leaf, impermeable to the recoil atoms but of sufficiently low stopping-power to the α-particles to be used as " source " together with the activized disk or foil.

By the remarkable experiments made by Sir Ernest Rutherford, partly in collaboration with Dr. J. Chadwick, the artificial disintegration of certain chemical elements has been achieved for the first time [*]. By the impact with the α-particles of high velocity from radium C and from thorium C, hydrogen nuclei of very long range have been expelled from the atoms of six of the lighter elements, viz., boron, nitrogen, fluorine, sodium, aluminium, and phosphorus. The other lighter elements up to calcium inclusive, as well as certain of the heavier elements, were tested for the same effect but with negative results.

Having at our disposal, thanks to the condensation method, means for obtaining very strong preparations of radium C, we decided to apply this method also for disintegration experiments with some of the lighter elements.

Our first objective was to study the magnetic deflexion of the H-particles from aluminium with a simple magnetic spectrometer constructed for that purpose. A narrow pencil of H-particles emerging through a slit between two blocks of lead is deflected away from the γ-rays by means of a strong magnetic field, the number of scintillations appearing on a zinc sulphide screen being counted by means of a microscope moved across the field by a micrometer screw. In order to obtain a high intensity of the H-radiation the source should have the same shape as the slit, and we therefore tried to modify the condensation method so as to condense the total amount of emanation on a narrow rectangular strip of aluminium foil, 1 by 10 mm. This proved to be a most difficult task, and a considerable number of different condensation vessels have been devised and tested without very satisfactory results. Finally, the first and simplest type of condensation vessel already described was reverted to, the steel stopper was covered with thin aluminium foil, which, when activized and freed from emanation, was folded into a narrow strip and pressed down into the groove of a screw-head made from aluminium. Using this as a source we were able to count the H-particles from aluminium at a distance between source and screen of 5 cm. and to observe their magnetic deflexion in a field of some 8000 gauss.

* Rutherford, Phil. Mag. xxxvii. p. 581 (1919) ; Bakerian Lecture, Proc. Roy. Soc. A, xcvii. p. 374 (1920); Rutherford and Chadwick, Phil. Mag. xlii. p. 809 (1921), *ibid.* xliv. p. 417 (1922).

As the H-particles from aluminium are not homogeneous, the range of the harder particles, according to Rutherford, varying between 30 and 90 cm. of air, the study of their magnetic deflexion practically requires the measuring out of a magnetic spectrum.   However, the rapid decay of radium C makes it unsuitable as a source, where prolonged measurements are required, and it therefore appeared most desirable to realize a source of H-particles of more constant activity.   A special type of condensation vessel, where frozen emanation itself, condensed on a narrow strip of copper, was to be used as source together with its fellow products under a cover of aluminium leaf, was constructed, but has so far not been put to actual tests, as a much simpler way of realizing the same objective was found in the meantime.

The Capillary Method.

From pieces of " hard" (potassium) glass tubing fine capillaries were drawn out, from 1 to 2 mm. thick and having walls, measured under the microscope, of between 70 and 90 μ.   The capillary was sealed up at one end, and over the next 10 mm. of its length the glass was lined inside with a thin sheet of the substance to be examined, equivalent in stopping power to about 2 cm. of air, either as a tiny roll of metal foil pressing well against the glass, or as a fine powder of oxide made to adhere to the glass through heating. An equal length of the glass was left bare for control measurements, and the capillary drawn thin over a short length, subsequently to be drawn out and sealed up after filling it with emanation, fig. 1.   The glass tubing with the

Fig. 1.

capillary was then joined to a recipient containing dry emanation mixed with some pure oxygen, which was introduced into the capillary after the latter had been sharply evacuated at a temperature of between 200° and 300° C., so as to remove moisture and absorbed gases.   The metal in the capillary had previously been bombarded with cathode rays in a high vacuum in order to remove occluded gases.   After sealing up the emanation within the capillary at nearly atmospheric pressure the latter was left for some hours and

its γ-activity measured, the equilibrium amount of radium C varying with different capillaries from 10 to 50 milligrammes.

The capillaries made in this manner are very convenient sources of H-particles from, say aluminium. They are easy to manipulate, have the practically linear shape suitable for deflexion experiments, and their use involves no risk of radioactive contamination, as the emanation they contain is hermetically enclosed. Their small dimensions and the way in which they are filled should be a safeguard against contaminations with hydrogen, free as well as in compounds, *i. e.* against the " natural " H-particles which form the most serious source of error in these experiments. Their chief advantage, however, is their constant activity, which declines with the half period of emanation itself, *i. e.* with 3·8 days instead of 20 minutes as with radium C, so that even prolonged measurements may be carried out without change of the source. On the other hand, it must be observed that the α-radiation within the capillary is not homogeneous, as α-particles of three different velocities are being discharged. Also there is some uncertainty about the distribution inside of the most effective component, *i. e.* of radium C. The latter distribution may, however, be changed at will by immersing one end of the capillary in liquid air until the total amount of radium C has accumulated in it.

Method of Observation.

The facilities offered by the method of the capillaries for studying the emission of H-particles from various substances appeared so considerable, that the study of the magnetic spectrum of the H-particles from aluminium was reserved for a future investigation. Instead, a number of capillaries were charged with some of the elements not investigated by Rutherford and Chadwick and were then examined for H-particles. The experimental arrangement is set out in fig. 2. C is the capillary, the unlined part of which is being examined, held by a carrier between the poles of a Leyboldt electromagnet. P_1 and P_2 are blocks of lead (in certain experiments of tungsten) jammed between the poles, which are 6 to 7 mm. apart. The lead serves as a screen against the radiation from the other part of the capillary. Similar blocks of lead P_3 and P_4 protect the eyes of the observer against the γ-radiation from the capillary. The scintillations appearing on the zinc sulphide screen Z are counted through the microscope M, whereas absorbing screens of different stopping power are introduced at A or, in some cases, laid

immediately over the capillary. The microscope closely resembles that described by Rutherford, the objective being a Watson holoscopic of 16 mm. focal length and numerical aperture 0·45, whereas the eyepiece is a wide-field ocular from Zeiss. Without diaphragm the field of view had a diameter of nearly 5 mm., so that the total area observed was practically 1/6 sq. cm. The light-gathering power of

Fig. 2.
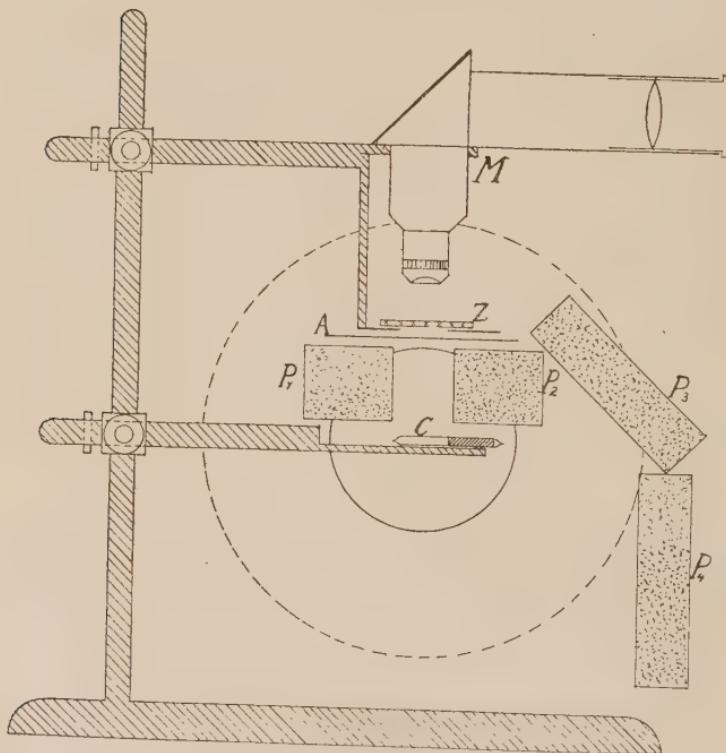
this microscope considerably exceeded that of any other combination tried by us. Nevertheless the scintillations produced by the H-particles are very faint, especially near the end of their range, so that the counting of scintillations, which was generally carried out at night, could not be made for more than one to two minutes at a time by each observer. When the scintillations were very numerous the period was limited to half a minute or even less. Three to

four counters alternated, their results being generally in good accordance with one another.

The quality of the screen is very important in these measurements. Most of the screens used we made ourselves from Sidot blende, but ready-made screens from Harrison Glew were also used with satisfactory results. The background of the screen was constantly illuminated by the γ-radiation from the capillary, which, however, seemed to vary considerably with the nature of the substance enclosing the emanation. With thin copper foil, used instead of the glass in experiments to be described later, the luminosity was much fainter than with glass, thus allowing the distance from source to screen to be considerably reduced.

Results with the Capillary Method.

The H-particles from aluminium are easily observed by the method just described. The number of penetrating H-particles found at different countings agrees well with the value given by Rutherford and Chadwick, *i.e.* about 2.10^{-6} Q, where Q is the total number of the impinging α-particles from radium C. Consequently with a field of view equal to ours, 1/6 sq. cm. at a distance of 15 mm. from source to screen, the number of scintillations observed from a capillary containing only one millicurie of emanation behind the aluminium lining should be about 20 per minute, provided the efficiency of the screen is equal to 0·75.

Control countings, when the unlined part of the glass capillary was examined, also gave a definite number of long range particles equal to about one-tenth of those from aluminium. These particles are, no doubt, expelled from sodium atoms in the glass. With capillaries drawn from " Jena Rotstrichglas " the number of these particles was considerably larger, in accordance with the composition of that glass, into which enter not only sodium but also certain amounts of boron and aluminium. Glass is therefore obviously not suitable as material for capillaries to be used for testing other elements for H-particles. For this reason we have instead drawn capillaries from pure fused silica, which is known to be quite free from impurities and which moreover presents the advantage that it can be very energetically heated, so as to drive off moisture and occluded gases from the substance with which it is charged before introducing the emanation.

Quartz capillaries drawn to the shape already described,

some 20 mm. in length, were coated inside over one half of their length with the following substances : scandium oxide, prepared from very pure oxalate of scandium, which had been kindly put at our disposal by Prof. R. I. Meyer of Berlin ; vanadium tetroxide, cobalt oxide, and arsenium, the latter element in the shape of a thin mirror, deposited inside the capillary by the Marsh procedure.   The last-named capillary could, of course, not be effectively heated, owing to the volatility of the metal.

The scintillations produced by these capillaries on a zinc sulphide screen at different absorptions were counted by means of the arrangement sketched in fig. 2.   The results proved, that *if* any H-particles at all of a range exceeding that of the natural particles are expelled from the atoms of these four elements, the ratio between their number, n, and that of the impinging α-particles, Q, is certainly less than 5 per cent. of the value for aluminium, *i. e.* $n/Q < 1 : 10^7$. A very small number of scintillations, from 1 to 2 per minute, was actually observed with an absorption equal to or exceeding 30 cm. of air with all these substances.   Owing to the scarcity of the particles producing these scintillations, their maximum range could not be determined, and it must be left for future investigations to explain their origin.

The number of scintillations appearing at lower values of the absorption down to about 11 cm. of air was, with two exceptions, practically the same, proving that hydrogen contaminations producing natural H-particles were practically absent from the capillaries.   One of these exceptions was the arsenium capillary, from which nearly 10 scintillations per minute were counted with an absorption of about 12 cm. air [*], whereas at 30 cm. the number was only a little more than 1 per minute.   Further experiments will have to be made with this element, but we are inclined to regard these scintillations as due to natural H-particles from hydrogen occluded by the metal.

The other exception was observed with the unlined part of the scandium capillary, which happened to be the most thin-walled of all, so that it could be examined with a total absorption of only 11 cm.   A relatively large number of

* Owing to the irregular shape of this capillary there is considerable uncertainty with regard to this value.   In view of later results, it does not appear impossible that these H-particles were expelled from the silicon atoms in the capillary walls.

scintillations of unmistakable H-particle type was then observed, viz. over 22 per minute, corresponding to a value of about $5 : 10^7$ for the quotient n/Q. This number was reduced to less than one-seventh, viz. 3 scintillations per minute, when the absorption was increased to 16 cm. of air by the introduction of a mica filter of 5 cm. air equivalent. This fact alone practically excludes the possibility that these scintillations could have been caused by natural H-particles from any hydrogen contamination within the capillary, which, moreover, would inevitably have given rise to similar particles also from the other part of the same capillary with its thin lining of scandium oxide, equal to about 2 cm. of air.

The only possible way of explaining these scintillations appears to be, that they are caused by H-nuclei expelled from the silicon atoms in the quartz. The other element present, viz. oxygen, has been examined by Rutherford for similar particles with negative results down to an absorption of 9 cm. of air, whereas with silicon the same test has only been carried down to the limit of 17 cm. We therefore infer from this result, which has since been confirmed with other quartz capillaries of still thinner walls, that the silicon atoms under intense bombardment with α-particles break down in a manner similar to that of the elements disintegrated in the experiments of Rutherford and Chadwick, emitting H-particles of the maximum range between 11 and 16 cm. of air. Owing to the difficulty of determining exactly the thickness and the air equivalent of the quartz walls of the capillaries used in these experiments, the numerical values just given are uncertain to a few cms of air. Experiments made by a somewhat different method and with elementary silicon instead of quartz, have made it possible to fix the maximal range of the H-particles from silicon more nearly at about 12 cm. of air.

Experiments with a Copper Foil Apparatus.

The unexpected results found with silicon forced us to give up quartz capillaries as suitable containers for disintegration experiments, where substances are to be tested for H-particles of short range. On the other hand, it appeared important to pursue that particular kind of investigation with some of the lighter elements found "non-active" in the experiments of Rutherford and Chadwick. We have therefore constructed a different kind of disintegration vessel,

where the thin silica wall of the capillaries is exchanged for a very thin membrane of pure copper[*].

In a brass piece, 2 mm. thick and 6 mm. broad, a slit 2 mm. wide and 45 mm. long is cut out. A strip of unperforated copper foil, about 11μ thick, is soldered over one opening of the slit thus forming a narrow trough, 2 by 2 by 45 mm. long, which can be hermetically closed by soldering a brass lid over its other opening. Four cross-pieces of brass are also soldered across the trough, dividing it into four compartments, which communicate with another by narrow slits immediately under the lid. Before soldering on the lid the substances to be studied are spread as uniformly as possible over the copper foil, one in each compartment, leaving only one compartment empty for control measurements. The area covered by each substance is thus 2 by 10 mm., and the average thickness of the layer is made equivalent in absorbing power to about 2 cm. of air. To charge this apparatus with emanation in the ordinary way by first evacuating it would expose the thin copper and the soldering to dangerous stress. It is therefore filled with emanation at ordinary pressure by means of the following contrivance. At one end the trough communicates with a minute brass mortar, in which a small glass capillary, sealed up with some 40 to 50 millicuries of dry radium emanation mixed with dry and pure oxygen, is crushed beneath a mercury seal by pushing home a small steel rod. At the other end the trough communicates through a fine tin tube with the atmosphere, so as to allow the excess air to escape when the capillary is being crushed. Immediately afterwards the tin tube is soldered off, enclosing the emanation from the crushed capillary hermetically within the trough, about 10 millicuries being enclosed within each compartment. The particles emerging downwards through the copper foil are counted from each division separately by an arrangement similar to that in fig. 2, save that the microscope with the zinc sulphide screen has to be mounted beneath the poles of the electromagnet and in inverted position, the objective directed upwards. As the air equivalent of the copper foil is less than the range of the α-particles from radium C, the latter are absorbed by filters of thin silver foil. These have previously been deprived of occluded gases, as has also the copper foil used in the

[*] A more complete description of this apparatus is published in the *Sitzungsberichte der Wiener Akademie der Wissenschaften* IIa, July 12th, 1923.

apparatus, by prolonged bombardment with cathode rays in a high vacuum. In order to remove all traces of hydrogen compounds the substances exposed within the trough have been heated and the trough itself, after being charged with the substances but before the emanation is introduced, has been washed out with a current of dry and warm oxygen.

The thin-drawn curves in fig. 3 represent the number of scintillations counted at different absorption values (produced by filters of thin mica) when the trough was charged with the following substances : beryllium oxide, magnesium oxide, and elementary silicon. The number of scintillations

Fig. 3.
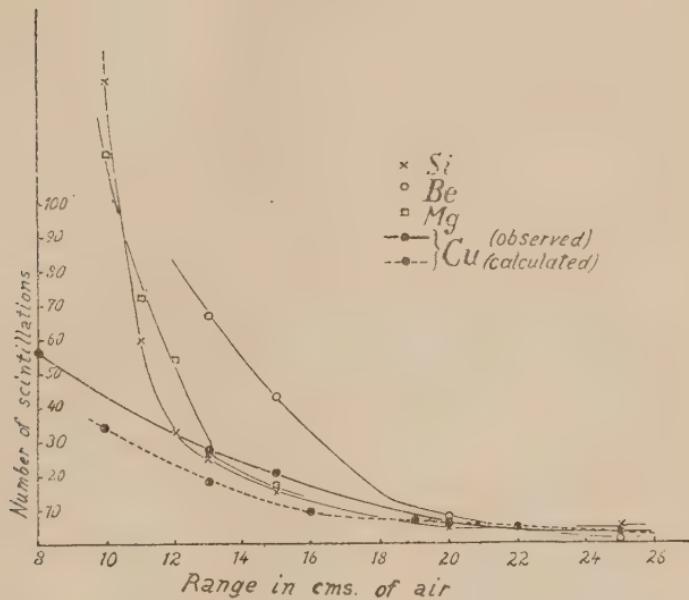
from the empty division, *i. e.* from the bare copper foil, is given by the full-drawn, thicker curve. At absorption values exceeding 20 cm. of air the latter curve is seen to coincide practically with the three first-named curves, whereas for absorption values less than 18 cm. the beryllium curve rises rapidly, and the same applies to the curves for magnesium and silicon at the absorption values 13 cm. and 12 cm. respectively. The conclusion appears to us unavoidable, that this considerable excess in number of short-range particles from the considered three elements over the similar particles from copper alone, must be due to H+particles expelled from

the atoms of Be, Mg, and Si by the α-particles discharged within the trough. Without regard to the absorption within the substances we may therefore say, that the three elements investigated have been found to give off H-particles of the approximate maximal ranges : Be, 18 cm. ; Mg, 13 cm.; and Si, 12 cm.

Regarding the particles from the bare copper foil the shape of their absorption curve does not seem to exclude the assumption that they may be due to traces of hydrogen contamination occluded in the metal and not completely driven off by the cathode rays. Thanks to the careful measurements made by Sir Ernest Rutherford on the absorption of natural H-particles expelled by α-particles of different velocities *, it is possible to compute a theoretical absorption curve for H-particles derived from such occluded hydrogen, under the assumption that this contamination is evenly distributed within the copper and with due regard to the fact that α-particles of three different initial velocities are active. The broken curve in fig. 3 represents a theoretical absorption curve for natural H-particles calculated in this manner, and drawn to such a scale that it coincides with the experimental curve for copper for absorption values exceeding 20 cm. of air. Also at lower absorption values the differences between the two latter curves are seen to be relatively small, considering that the theoretical curve cannot be very exactly defined. If, on the other hand, the hydrogen contamination were assumed to be differently localized within the copper, or to occur only over its inner surface, the theoretical curves, which can then be calculated, are very similar to the broken curve in the diagram. Whether there are any H-particles of a range exceeding 8 cm. of air expelled from copper atoms or not, must at present be left an open question. Anyhow, it seems hardly possible to attribute the large excess in the H-particles of shorter range expelled from the charged divisions over those from copper alone to any other reason than a disintegration of the atoms in the substances.

It may be added, that a much larger number of scintillations was observed from the three elements investigated, at a minimal value of absorption equal to 8 cm. of air, namely, from beryllium about 400 per minute, and from magnesium and silicon between 250 and 300 per minute. These numbers being too large for direct countings, they were instead estimated independently by the different observers, and an

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* Rutherford, Phil. Mag. xxxvii. p. 550 (1919).

average value was formed.   The corresponding points are
not set out in the diagram, partly for want of space, partly,
also, owing to the higher degree of uncertainty of these
estimated numbers.

   In another series of similar measurements the trough was
charged with carbonate of lithium, sulphide of copper, and
chloride of silver, one division being as usual left bare for
control.   The number of scintillations from this division was,
however, at these experiments considerably larger than before,
probably owing to a stronger contamination by occluded
hydrogen, so that no definite results could be inferred with
regard to sulphur and chlorine.   For lithium the results
appeared to establish as fairly certain the emission of
H-particles of the maximum range equal to some 10 cm.
of air.

   In the following table the results hitherto obtained with
regard to atomic disintegration by α-particles are set out,
according to our own experiments as well as to those of
Rutherford and Chadwick.   The ranges of the expelled
H-particles given in the second column refer to particles in
the forward direction.   Whether the elements disintegrated
by us emit particles also in the backward direction has not
yet been investigated.

   Judging by analogy with Rutherford's results, the range
of such backward particles should be considerably less than
that of those directed forwards and correspondingly more
difficult to investigate.

TABLE I.

Element.	Atomic number.	Atomic mass.	Range of H-particles.
Lithium	3	6 : 7	10 cm.
Beryllium	4	9	18 cm.
Boron	5	10 : 11	58 cm.*
Nitrogen..................	7	14	40 cm.*
Fluorine..................	9	19	65 cm.*
Sodium	11	23	58 cm.*
Magnesium	12	24 : 25 : 26	13 cm.
Aluminium	13	27	90 cm.*
Silicon	14	28 : 29	12 cm.
Phosphorus	15	31	65 cm.*

   * According to Rutherford and Chadwick, Phil. Mag. xliv. p. 425.

Future Investigations.

The methods described in this paper offer facilities for further research on atomic disintegration. With an apparatus similar to the one last described, the different elements of the periodic system may be investigated for H-particles of a range barely exceeding that of the α-particles from radium C, possibly, with the aid of a strong magnetic field, also for particles of still shorter range.

Preparations are being made in this Institute to utilize the method of capillaries for making the H-rays from aluminium and from other disintegrable elements visible by the Wilson method. It is to be hoped that one may in this way also be able to decide, whether one or more H-particles are expelled from the same disintegrating atom.

We wish, in conclusion, to express our sincerest gratitude to Professor Stefan Meyer for generously putting the resources of the Radium Institute at our disposal, as well as for the kind interest he has taken in our research.

Summary.

A new method for obtaining strong preparations of radium C from radium emanation by condensation with liquid air is described.

Two different methods have been worked out for studying the particles expelled from artificially disintegrated atoms.

The elements Sc, Va, Co, and As have been investigated for H-particles of a range exceeding about 17 cm. of air, the results proving that such particles, if expelled at all, are certainly less numerous than one-twentieth of the particles expelled from aluminium.

As a first result of the same methods applied to the study of short-range particles, the following three elements have been found to give off H-particles under bombardment with α-particles, namely : beryllium, magnesium, and silicon, whereas for lithium the evidence of disintegration is less conclusive.

Some lines for further research are indicated.

XLIII. *The Molecular Association of Liquids and Highly-Compressed Gases.* — *Part* III. *The Molecular Association of Liquids. By* E. E. WALKER, *D.Sc., D.I.C., A.C.G.I.**

ACCORDING to the law of corresponding states the critical coefficient $\left(\dfrac{d\pi}{d\theta}\right)_c$ should be the same for all substances. Van der Waals has shown that, though this is not strictly the case, it † is a function of the ratios $\dfrac{RT_c}{P_c V_c}$. In Part I.‡ it was shown that this ratio is a function of the length of the molecule, and it follows from this that $\left(\dfrac{d\pi}{d\theta}\right)_c$ is also a function of this quantity. Many authors have pointed out that this coefficient and the related coefficient "*f*," which is defined by the equation

$$f = \frac{\log \dfrac{1}{\pi}}{\dfrac{1}{\theta} - 1},$$

are dependent on the size of the molecule, and that only substances of approximately the same molecular size obey the law of corresponding states, but its correlation with the length of the molecule makes it possible to give the conception quantitative form. In fact, one may restate the law of corresponding states as follows :—

The relationships existing between the true reduced temperatures, pressures, and volumes of all substances, the molecules of which have the same length, are very nearly identical.

Before proceeding to examine the validity of this statement, it is necessary to explain what is meant by the terms "true reduced temperatures, pressures, and volumes." The reduced coordinates of an unassociated substance are respectively $\dfrac{T}{T_c}$, $\dfrac{P}{P_c}$, and $\dfrac{V}{V_c}$. In the case of associated substances these simple ratios give only the apparent reduced coordinates. To obtain the true reduced quantities it is

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necessary to substitute for T_c, P_c, and V_c those critical constants which would have been observed if the liquid could have been raised from the temperature T to the critical point without any change in the equilibrium between the simple and associated molecules. In Part II.* a method of estimating the effect of varying degrees of association on the critical constants was devised, and the equations deduced in that paper may be used to calculate the true reduced coordinates of an associated substance.

Let θ_a, π_a, V_a be the apparent reduced coordinates,

θ_t, π_t, V_t be the true reduced coordinates,

n be the association factor at a given temperature,

and n_c be the association factor at the critical point,

then by equations (6), (7), and (8) of Part II. :—

$$\theta_t = \theta_a \times \left(\frac{n}{n_c}\right)^{-\frac{1}{3}-x+\frac{2}{3}y}, \quad \cdots \cdots \quad (1)$$

$$\pi_t = \pi_a \times \left(\frac{n}{n_c}\right)^{+\frac{2}{3}+x+\frac{5}{3}y}, \quad \cdots \cdots \quad (2)$$

$$V_t = V_a \times \left(\frac{n}{n_c}\right)^{-x-y}. \quad \cdots \cdots \quad (3)$$

x and y have been defined in Parts I. and II. They may be calculated from the length of the molecule as follows :—

$$x = 3\cdot33 \log_{10}\frac{\cdot838 + \cdot174 \log_{10} 2l}{\cdot838 + \cdot174 \log_{10} l},$$

$$y = 3\cdot33 \log_{10}\frac{1 + \dfrac{12\cdot2}{8l^3}}{1 + \dfrac{12\cdot2}{l^3}}.$$

If the modified law of corresponding states holds good for liquids containing simple and associated molecules in equilibrium, then it should be possible to determine $\dfrac{n}{n_c}$ for any given liquid by equating its true reduced coordinates with those of a saturated normal paraffin having a molecular length equal to the average molecular length $(n \times l)$ of the associated substance. For the present it will be assumed that the modified law holds good both for associated and

unassociated liquids, and the validity of this hypothesis must be judged after an examination of the results achieved by its application to the problem of molecular association.

In order to obtain values of $\frac{n}{n_c}$ for an associated liquid, any two of the three coordinates may be chosen and equated with the corresponding coordinates of a normal paraffin having the same molecular length. The necessary data for the lower paraffins are, however, scanty, and those for the vapour-pressure curves are most easily interpolated. It is on this account that the first calculations have been made from temperatures and vapour pressures.

The reduced temperature of any liquid normal paraffin may be calculated with sufficient accuracy from the expression :

$$\theta = \frac{\theta_p}{1 - C(1 - \theta_p)}.$$

Where θ is the reduced temperature of the liquid and θ_p is the reduced temperature of normal pentane under the same reduced pressure. The values of C found for various normal paraffins are given in Table I.

TABLE I.

|	C.	l.	C.
Methane	$-\cdot222$*	3	$-\cdot220$
Ethane	$-\cdot152$	4	$-\cdot175$
Propane	$-\cdot0943$	5	$-\cdot135$
Butane	$-\cdot045$	6	$-\cdot099$
Pentane	$\pm\cdot0000$	7	$-\cdot066$
Hexane	$+\cdot0398$	8	$-\cdot035$
Heptane	$+\cdot0772$	9	$-\cdot006$
Octane	$+\cdot1062$	10	$+\cdot021$
		11	$+\cdot046$
		12	$+\cdot070$
		13	$+\cdot097$
		14	$+\cdot109$

* By extrapolation.

Values of C corresponding with various integral molecular lengths have been determined from these data by graphical interpolation, and are recorded in the same table. From these values and Young's data for pentane, curves can be constructed connecting true reduced temperatures (θ_t) with true reduced pressures (π_t) for any length of molecule. In

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the case of an associated substance the problem is to find what value of $\frac{n}{n_c}$ will satisfy equations (1) and (2). This can be solved by the following graphical construction.

Values of $\log \frac{1}{\pi_t}$ are plotted as ordinates against values of $\log \frac{1}{\theta_t}$ as abscissæ for various lengths of molecule. A similar $\log \frac{1}{\pi_a}$, $\log \frac{1}{\theta_a}$ curve is plotted for the associated substance.

Fig. 1.
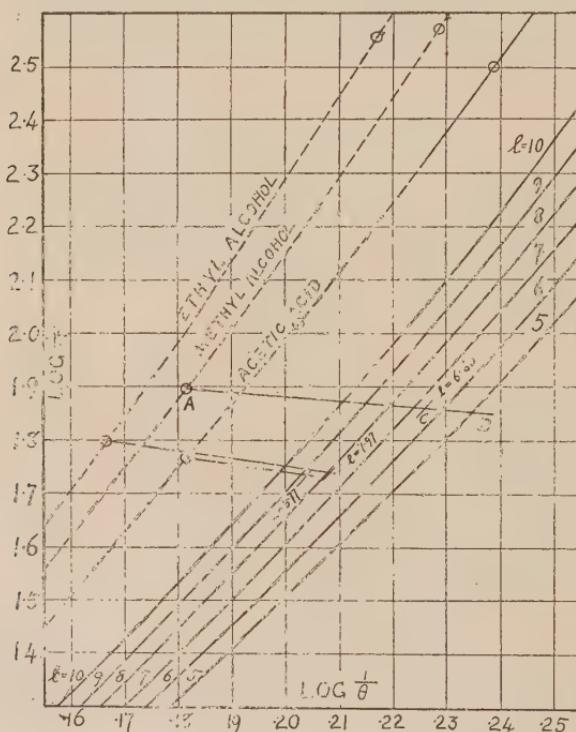
Portions of these curves are shown in fig. 1, the dotted curves being for methyl alcohol, ethyl alcohol, and acetic acid. Through any required point A on the desired curve a straight line AB is drawn with a slope of

$$\frac{-\frac{1}{3} - x + \frac{2}{3}y}{+\frac{2}{3} + x + \frac{3}{3}y}.$$

The point C representing the logarithms of the true reduced

coordinates of the associated substance must be on this line, and it must be also on the $\log\frac{1}{\pi_t}$, $\log\frac{1}{\theta_t}$ curve for a substance of molecular length equal to $n \times l$. This point can be fixed by means of a few trials without any difficulty. Fig. 1 represents part of the diagram used in determining the association factors of ethyl alcohol and acetic acid at various temperatures.

Values of $\frac{n}{n_c}$ for the saturated normal paraffins are necessarily unity by this method, since they are chosen as the standards against which all other substances are compared. Values of $\frac{n}{n_c}$ for other hydrocarbons at the atmospheric boiling-point are recorded in Table II. According to these,

TABLE II.

	$l.$	$-\frac{1}{3}-x+\frac{2}{3}y.$	$+\frac{2}{3}+x+\frac{5}{3}y.$	$n_c.$	$\dfrac{n_b}{n_c}.$	$n_b.$
Normal paraffins.	...	...	...	1·00	1·00	1·00
Iso-pentane	7·56	−·431	+·683	1·005	1·017	1·02
Di-iso-propyl......	7·56	·431	·683	1·007	1·030	1·035
Di-iso-butyl	10·74	·415	·718	1·00	1·024	1·025
Hexamethylene...	7·30	·432	·675	1·00.	1·019	1·02
Benzene	7·30	·432	·675	1·012	1·017	1·03
Acetylene	4·58	·511	·492	...	1·061	...
Ethylene ...,.....	4·58	·511	·492	...	·996	...

"iso"-structure induces traces of association. It cannot be stated for certain that these traces of association are genuine, they might be due to inaccuracies in the modified law of corresponding states. If this is so, the errors are not large. It may be mentioned, however, that the addition of methyl groups as a rule enhances molecular association, and therefore these traces of association may well be genuine. Acetylene is quite appreciably associated but ethylene is not, the critical volumes of these substances are not known, so that n_c cannot be calculated with accuracy, but an examination of the other critical constants indicates that acetylene is more highly associated than ethylene at the critical point. In this and succeeding tables it should be noted that the value of $\frac{n_b}{n_c}$ is never appreciably * less than unity, thus

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* Ethylene is the only case which has been observed, but this may be regarded as unity within experimental error.

justifying the selection of the normal paraffins as comparison substances. Whether they are associated or not, they appear to be the least associated of all substances.

Similar data for a variety of slightly associated organic compounds are recorded in Table III. It will be observed

TABLE III.

	$l.$	$-\frac{1}{3}-x+\frac{2}{3}y.$	$+\frac{2}{3}+x+\frac{5}{3}y.$	$n_c.$	$\dfrac{n_b}{n_c}.$	$n_b.$
Methyl formate......	6·43	− ·447	+ ·649	1·062	1·053	1·12
Ethyl formate	7·97	·427	·691	1·041	1·037	1·08
Propyl formate......	9·51	·418	·710	1·022	1·032	1·055
Methyl acetate	7·42	·433	·680	1·057	1·065	1·125
Ethyl acetate.........	8·96	·421	·703	1·046	1·055	1·105
Propyl acetate	10·50	·415	·718	1·031	1·043	1·075
Methyl propionate..	8·96	·421	·703	1·035	1·051	1·09
Ethyl propionate ...	10·50	·415	·718	1·028	1·039	1·07
Methyl butyrate ...	10·50	·415	·718	1·023	1·037	1·06
Methyl-iso-butyrate	8·96	·421	·703	1·025	1·052	1·08
Ethyl ether	8·96	·421	·703	1·012	1·019	1·03
Methyl chloride ...	4·39	·523	·461	1·065	1·042	1·11
Carbon tetrachloride	5·74	·461	·611	1·010	1·024	1·035
Stannic chloride ...	7·00	·438	·669	1·011·	1·032	1·045
Fluorbenzene.........	7·90	·427	·691	1·017	1·022	1·04

that the degree of association at the boiling-point is, as a rule, approximately twice that at the critical point. Among isomeric esters the acetates are more highly associated than either the formates, propionates, or butyrates. The methyl group appears to exert a specific influence in this and other cases. Thus, for example, methyl chloride is more highly associated than carbon tetrachloride.

TABLE IV.

	$l.$	$-\frac{1}{3}-x+\frac{2}{3}y.$	$+\frac{2}{3}+x+\frac{5}{3}y.$	$n_c.$	$\dfrac{n_b}{n_c}.$	$nb.$
Methyl alcohol	4·34	− ·527	+ ·451	1·259	1·214	1·53
Ethyl alcohol	5·88	− ·459	+ ·620	1·097	1·233	1·355
Propyl alcohol	7·42	− ·433	+ ·650	1·072	1·189	1·275
Acetic acid............	5·88	− ·459	+ ·620	1·341	1·118	1·49
Acetonitrile	5·13	− ·483	+ ·562	1·470	1·077	1·585
Proprionitrile	6·67	− ·442	+ ·657	1·305	1·030	1·345
Water.................	2·80	− ·782	− ·174	1·270	1·12	1·42
Ammonia	2·80	− ·782	− ·174	1·091	1·11	1·21
Hydrogen chloride .	2·85	− ·768	− ·141	1·057	1·40	1·48

Data for more highly associated substances are recorded in Table IV. Among these substances there is no clear

relationship between the degree of association at the boiling-point and that at the critical point, though the nitriles are peculiar in that, although they are highly associated at the critical point, they are only very slightly more associated at the boiling-point. This fact appears to account for certain peculiarities of these substances. Some methods indicate that they are normal substances, and others that they are associated [*]. Thus the Trouton constant for the nitriles is practically normal and their rectilinear diameter is remarkably straight. The table shows that this method of measuring molecular association is in agreement with the Rose Innes surface-tension method in indicating that methyl alcohol is more associated than water. Walden's molecular cohesion method gives the same result, and it seems that in this case also the methyl group is exerting a specific influence.

The method is applicable to all temperatures, and the association factors have been worked out over a wide range of temperatures for the alcohols and acetic acid. The values

TABLE V.

Methyl alcohol.			Ethyl alcohol.		
t.	$\dfrac{n}{n_c}$.	n.	t.	$\dfrac{n}{n_c}$.	n.
30	1·258	1·584	40	1·291	1·416
64·7 B.P.	1·214	1·528	78·3 B.P.	1·235	1·354
100	1·171	1·474	110	1·184	1·299
130	1·135	1·429	150	1·126	1·235
180	1·070	1·347	180	1·079	1·182
220	1·023	1·288	220	1·028	1·128
234	1·007	1·268	230	1·017	1·116
238	1·002	1 262	240	1·002	1·099
240·0 C.	1·000	1·259	243·1 C.	1·000	1·097

Propyl alcohol.			Acetic acid.		
40	1·279	1·371	70	1·132	1·518
60	1·249	1·339	100	1·124	1·507
97·4 B.P.	1·189	1·275	118·5 B.P.	1·118	1·491
150	1·115	1·195	150	1·100	1·489
200	1·053	1·129	200	1·076	1·443
240	1·019	1·092	250	1·051	1·409
260	1·004	1·076	280	1·024	1·373
263·7 C.	1·000	1·072	300	1·014	1·360
			310	1·008	1·352
			321·6 C.	1·000	1·341

[*] See Ter Gazarian, *J. Chim. Phys.* iv. p. 140 (1906).

are recorded in Table V., and are plotted against temperature in fig. 2. It is very surprising that the rapid change in volume which takes place in the neighbourhood of the critical point should not produce a correspondingly marked change in the association factor. It appears that in this highly condensed state the volume has but little influence on the degree of association which is almost solely a function of the temperature.

Fig. 2.
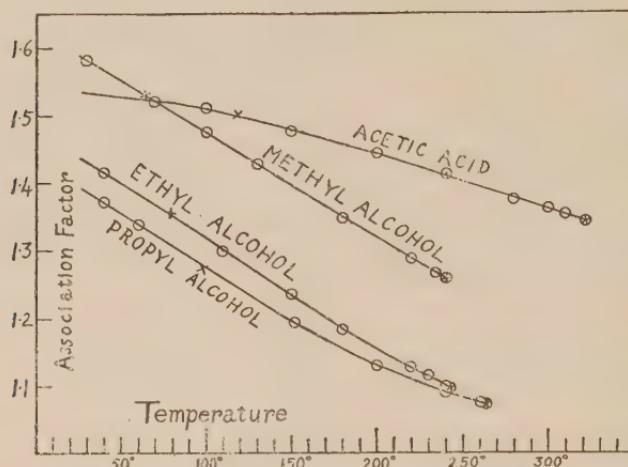
Curves showing variation of association factors with temperature.
× indicates boiling-point.
⊕ indicates critical point.

It has been pointed out that, if the modified law of corresponding states is true generally, it should be possible to determine the association factor from any two reduced coordinates. Thus, it should be possible to determine $\frac{n}{n_c}$ from the apparent reduced volumes and apparent reduced temperatures. An attempt has been made to do this, using equations 2 and 3 and employing a method somewhat similar to that just described. The results are, however, vitiated by the fact that only scanty data are available for the lower paraffins. These data are less easy to interpolate than the vapour-pressure data, and somewhat doubtful extrapolation has been necessary in some cases. The method will not be described here in detail, as it is hoped that it may be found possible to improve it, but some results which have been obtained are quoted in Table VI., as they give considerable

TABLE VI.

Apparent reduced volume.	Acetic Acid.			Methyl Alcohol.			Ethyl Alcohol.		
	Temperature.	Volume method. n	Vapour-pressure method. n	Temperature.	Volume method. n	Vapour-pressure method. n	Temperature.	Volume method. n	Vapour-pressure method. n
·38	130·7	1·47	1·49	98·0	1·53	1·48	89·9	1·34	1·34
·40	164·8	1·46	1·47	127·3	1·52	1·43	122·8	1·33	1·28
·45	228·6	1·42	1·42	176·3	1·44	1·35	172·5	1·24	1·20
·55	288·8	1·37	1·37	218·8	1·32	1·29	218·3	1·14	1·12
·75	...	...	...	238·5	1·27	1·26	242·2	1·11	1·10
1·00	321·6	1·34	1·34	240·0	1·26	1·26	243·1	1·10	1·10

support to the hypothesis which forms the basis of this communication. The association factors calculated by the two methods are on the whole in good agreement, and, though the values calculated from reduced volumes must be regarded as provisional, they afford valuable evidence in support of the main contentions put forward in this paper. So far as the author is aware, there is no reason why this measure of agreement should be obtained unless

(*a*) The modified law of corresponding states holds good for these associated substances.

(*b*) The method of calculating the true reduced coordinates is true as a first approximation.

No such measure of agreement would be obtained if the hypothesis were altered in any important particular. Thus, for instance, in calculating the true reduced coordinates, it was assumed (see Part II., *loc. cit.*) that the molecules are joined end to end, so that the length of a double molecule is twice that of a single one. If the assumption is made that the molecules are joined side by side, so that the length of a double molecule is the same as that of a single one, the calculation of the true reduced coordinates becomes very much simplified, since x and y in equations (1), (2), and (3) become equal to zero. The association factors calculated on this hypothesis are considerably higher, and the agreement between the two methods is distinctly less satisfactory.

TABLE VII.

	Methyl alcohol. n	Ethyl alcohol. n	Acetic acid. n	
Vapour-pressure method.	1·81	1·53	1·78	Molecules side by side, x & $y=0$, Mean divergence=11·6 per cent.
Volume method	2·22	1·43	1·67	
Vapour-pressure method.	1·48	1·34	1·49	Molecules end to end, x & y corrections used. Mean divergence=1·6 per cent.
Volume method	1·53	1·34	1·47	

The association factors of methyl alcohol, ethyl alcohol, and acetic acid at an apparent reduced volume of 0·38 have been calculated on this alternative hypothesis, and are recorded in Table VII. The mean divergence between the results given by the volume and vapour-pressure methods is raised

from 1·6 per cent. to 11·6 per cent. This increased divergence is striking in the case of methyl alcohol, but is less marked in the other two cases. It appears, therefore, that the adoption of the more probable hypothesis is justified in spite of the greater complexity which it introduces into the calculations.

It now remains to consider how far the results obtained have justified the modification of the law of corresponding states proposed in this paper. Firstly, the association factors calculated on the basis of this hypothesis are rational and free from obvious anomalies. Secondly, two different methods of determining the association factor, depending on different physical properties, give values which are in good agreement with one another. A third argument in its favour is the difficulty of finding any reasonable alternative hypothesis. If, for instance, it is assumed that isomers are corresponding substances, then such substances as isopentane, di-iso-propyl, and di-iso-butyl would appear to be actually dissociate l, their association factors at the boiling-point being several per cent. less than unity, and becoming smaller as the temperature fails. Moreover, we should be left without a guide in the case of substances not isomeric with the normal paraffins. Similar anomalies are observed if it is assumed that substances of equal molecular weight or equal molecular volume obey the law of corresponding states. Sometimes it is stated that substances having equal or nearly equal critical temperatures are corresponding substances, but further anomalies are met with in this case. Iso-pentane, di-iso-propyl, di-iso-butyl, hexamethylene, benzene, carbon tetrachloride, and various other substances would appear to be dissociated, and mercury (which cannot be dissociated) would prove a glaring exception, for its reduced vapour-pressure curve corresponds with those of the monatomic gases, a fact which is in harmony with the hypothesis put forward in this paper, but is entirely contrary to what would be expected if critical temperature or molecular weight were the controlling factor. The association factors calculated in this paper are entirely free from such anomalies, and, though n_b is sometimes only one per cent. greater than n_c, no case has been observed in which it is appreciably less. It cannot be doubted that other dimensions of the molecule besides the length exert some influence on the true reduced coordinates, and that only those substances having exactly the s me molecular dimensions are likely to correspond exactly, but the influence of the length appears to be paramount and that of the other dimensions must be small. It is believed,

therefore, that the modified law of corresponding states is a reasonably close approximation to the truth, and that the association factors which have been calculated by means of this hypothesis are at least more reliable than any which have been determined up to the present.

One alternative suggestion as to the exact physical meaning of "*l*" may be put forward here, though it cannot be tested satisfactorily from existing data. It seems probable that "*l*" may represent not merely the length of the molecule but the mean collision area. In the case of normal carbon chains the mean collision area would be very nearly proportional to the length. Side chain formation and ring formation would reduce the mean collision area, though not quite in the same ratio as the reduction in the molecular length. It is possible that the conventionally determined molecular length used in these papers is really a rough estimate of the mean collision area. This could be tested by extensive viscosity measurements on substances belonging to isomeric and homologous series.

The thirty pure instances investigated by Young and his collaborators form the backbone of the experimental data quoted in these three papers. Outside these authors' work there are probably very few critical volumes of organic compounds that can be relied upon. The critical volumes of methane *, methyl chloride, and the nitriles, determined respectively by Cardoso, Baume, and Ter Gazarian, are probably accurate, and all these values have been employed. The only really doubtful critical data which have been used are those for propane † and ammonia. It is hoped that some laboratory equipped for low-temperature research will undertake a thorough study of the lower paraffins comparable with that carried out by Young on pentane, hexane, heptane, octane, and some of their isomers. Such work would fill in an important gap in our knowledge and provide data for

* At the time this paper was written the author was not acquainted with the recent work of Keyes on methane (Journal of Maths. and Physics, Massachusetts Inst. of Technology, August 1922). This work confirms Cardoso's critical constants on the whole, but points out a slight error in his temperature-scale.

† It is found that the critical pressures determined by the older workers—Olzewsky, Nadejine, Altschul, and others—are from two to six per cent. too high. Olzewsky's value for ethane is 2 per cent. high, therefore in these papers it has been assumed that his value for propane is also 2 per cent. high, and in all calculations in these papers the value 43·1 atmospheres has been used instead of the experimental value 44·0. There can be no doubt that the assumed value is very close to the truth. No other critical pressures determined by these authors have been employed in these papers.

determining with greater accuracy the association factors of such highly associated substances as water and ammonia, which, having small molecules themselves, must necessarily be compared with the lower paraffins.

Summary.

A modified law of corresponding states has been proposed. This law indicates that only substances the molecules of which have the same length (or possibly the same mean collision area) are truly corresponding substances. It is shown that this law is applicable to associated substances if proper correction is made for the effect of molecular association on the critical constants. By means of this modified law of corresponding states the association factors of twenty-four substances at the boiling-point have been determined, and these calculations have been extended over a wide range of temperature in the case of the alcohols and acetic acid.

XLIV. *The Influence of the Earth's Rotation on a Top.* By JOHN LIGHTON SYNGE, *M.A.*[*]

THE rotation of the plane of vibration of a pendulum due to the earth's rotation was deduced by Foucault, not on the basis of classical mechanics, but from the empirical assumption that the normal to the plane of vibration tends to set itself as parallel as possible to the earth's axis ('Travaux Scientifiques,' p. 382). The application of the same principle to the case of a top rotating on the earth's surface led him at once to the following conclusions:—" If one considers the rotation of the earth, one finds that the position of a top in motion is not that in which its axis coincides with the vertical, but that it corresponds to a certain oblique line contained in the plane of the meridian and which leans south or north according as the top turns to the right or to the left. It is impossible to give the value of the angle which measures the inclination of the top, seeing that this angle varies with the form, the mass, and the velocity of rotation of the apparatus. All one can say is that it increases with the rapidity of the motion, with the moment of inertia of the system, and with the lowering of its centre of gravity below the point of support." (*Op. cit.* p. 410.) He proceeds

[*] Communicated by the Author.

to describe the apparatus which he employed to observe this effect, states that he observed it, but leaves a blank in the space destined for a quantitative result.

He predicts further that if a top be spun on a horizontal glass plate it will travel from west to east. This is a direct consequence of his previous prediction, for if the axis of the top is inclined to the vertical, the horizontal plane makes contact with the top around a small circle, and the rolling of this small circle on the plane will produce the effect described. He states that he observed this effect, but again the space destined for a quantitative result is left blank.

The object of the present paper is to show, as a result of rigorous treatment, that the effect of the earth's rotation is the reverse of that predicted by Foucault : that for earth-like rotation the inclination is to the south, for the contrary rotation to the north, and thus the direction of travel for either sense of rotation is not from west to east, but from east to west.

Let G be the centre of gravity of the top, V its vertex, and let $VG = a$; let M be its mass, and A, A, C the principal moments of inertia at G. We regard V as a point fixed relative to the earth's surface. Let O be the projection of V on the earth's axis ; OZ the earth's axis in the sense south–north; OX, OY fixed directions forming a right-handed system of rectangular axes. Let NV be the direction of the earth's gravitational field at V, and let α be the angle between VN and OZ. Since the top is small, we may regard the earth's field as parallel to NV of uniform intensity g. Let $OV = \rho$. Let (x, y, z) be the coordinates of G, and (θ, ϕ, ψ) Eulerian angles specifying the orientation of the top relative to (OXYZ).

The kinetic energy is given by

$$T = \tfrac{1}{2}M(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + \tfrac{1}{2}A(\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta) + \tfrac{1}{2}C(\dot{\psi} + \dot{\phi} \cos \theta)^2,$$

and the potential energy is Mgp where p is the projection of VG on VN, or

$$p = a \sin \theta \sin \alpha \cos (\phi - \Omega t) + a \cos \theta \cos \alpha,$$

where Ω is the angular velocity of the earth and $y = 0$ is the meridian plane through V when $t = 0$. We have

$$x = \rho \cos \Omega t + a \sin \theta \cos \phi,$$
$$y = \rho \sin \Omega t + a \sin \theta \sin \phi,$$
$$z = a \cos \theta,$$

Substitution gives

$$L = T - V = \tfrac{1}{2}M\rho^2\Omega^2 + \tfrac{1}{2}A'(\dot{\theta}^2 + \dot{\phi}^2 \sin^2\theta) + \tfrac{1}{2}C(\dot{\psi} + \dot{\phi}\cos\theta)^2$$
$$+ M\rho\Omega a[\dot{\theta}\cos\theta\sin(\phi - \Omega t) + \dot{\phi}\sin\theta\cos(\phi - \Omega t)]$$
$$- Mga[\sin\theta\sin\alpha\cos(\phi - \Omega t) + \cos\theta\cos\alpha],$$

where A' is the moment of inertia about an axis through V perpendicular to the axis of symmetry. The system is holonomic, specified by coordinates θ, ϕ, ψ, of which ψ is ignorable : thus we have the integral

$$\frac{\partial L}{\partial\dot{\psi}} = C(\dot{\psi} + \dot{\phi}\cos\theta) = \beta, \text{ a constant.}$$

The modified kinetic potential, omitting constants, is

$$R = \tfrac{1}{2}A'(\dot{\theta}^2 + \dot{\phi}^2 \sin^2\theta) + \dot{\phi}\beta\cos\theta$$
$$+ M\rho\Omega a[\dot{\theta}\cos\theta\sin(\phi - \Omega t) + \dot{\phi}\sin\theta\cos(\phi - \Omega t)]$$
$$- Mga[\sin\theta\sin\alpha\cos(\phi - \Omega t) + \cos\theta\cos\alpha].$$

The equations of motion,

$$\frac{d}{dt}\left(\frac{\partial R}{\partial\dot{\theta}}\right) - \frac{\partial R}{\partial\theta} = 0, \quad \frac{d}{dt}\left(\frac{\partial R}{\partial\dot{\phi}}\right) - \frac{\partial R}{\partial\phi} = 0,$$

become

$$A'(\ddot{\theta} - \dot{\phi}^2 \sin\theta\cos\theta) + \beta\dot{\phi}\sin\theta - M\rho\Omega^2 a\cos\theta\cos(\phi - \Omega t)$$
$$+ Mga[\cos\theta\sin\alpha\cos(\phi - \Omega t) - \sin\theta\cos\alpha] = 0,$$
$$A'(\ddot{\phi}\sin^2\theta + 2\dot{\theta}\dot{\phi}\sin\theta\cos\theta) - \beta\dot{\theta}\sin\theta$$
$$+ M\rho\Omega^2 a\sin\theta\sin(\phi - \Omega t)$$
$$- Mga\sin\theta\sin\alpha\sin(\phi - \Omega t) = 0.$$

The steady motion will be given by these equations on putting $\theta = $ constant, $\phi = \Omega t$: we find

$$- A'\Omega^2 \sin\theta\cos\theta + \beta\Omega\sin\theta - M\rho\Omega^2 a\cos\theta$$
$$+ Mga\sin(\alpha - \theta) = 0$$

from the first equation, while the second equation is satisfied identically.

So far we have used no approximation, but now, remembering that Ω is small (while ρ is large), we may omit the first term, and substituting $C\omega$ for β, where ω is the angular velocity of the top about its axis, we obtain

$$Mga\sin(\theta - \alpha) = C\omega\Omega\sin\theta - M\rho\Omega^2 a\cos\theta . \quad . \quad (1)$$

If $\theta = \theta_0$ when $\dot{\omega} = 0$, then θ_0 defines the vertical direction of the plumb-line or of the normal to a liquid surface, which Foucault used as a surface of comparison. Then

$$\mathrm{M}ga \sin (\theta_0 - \alpha) = -\mathrm{M}\rho\Omega^2 a \cos \theta_0.$$

Elimination of the last terms gives

$$\mathrm{M}ga \cos \alpha \sin (\theta - \theta_0) = \mathrm{C}\omega\Omega \sin \theta \cos \theta_0,$$

or since θ, θ_0, α are approximately equal, and α is the complement of the latitude λ,

$$\theta - \theta_0 = \frac{\mathrm{C}\omega\Omega \cos \lambda}{\mathrm{M}ga}.$$

Thus according as ω, Ω have the same or opposite signs, $\theta >$ or $< \theta_0$, that is, the deviation is to the south or to the north: hence the direction of travel on a horizontal plate is from east to west.
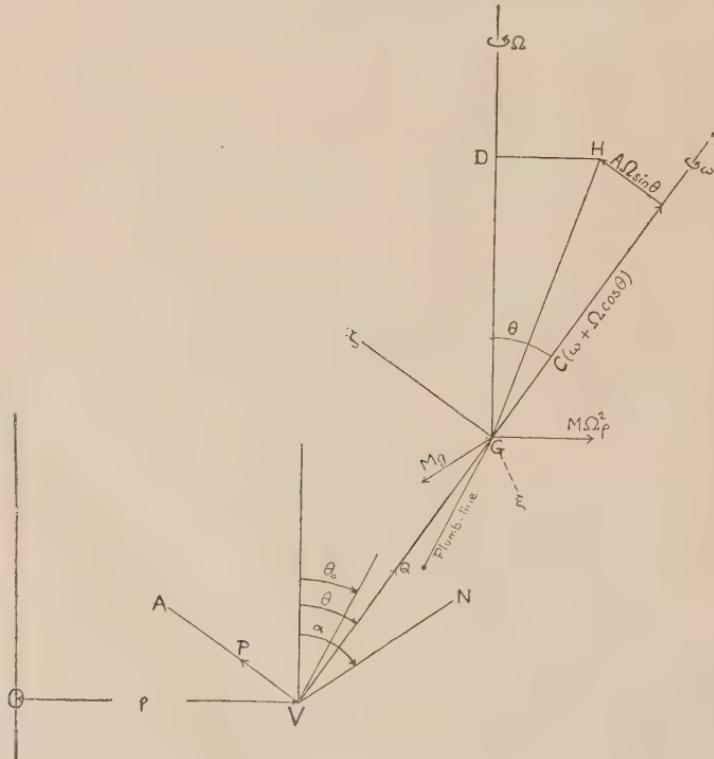
The same result may be obtained more obviously by a graphical method. The diagram shows the case of an earth-like rotation. A particle of mass M at G is in statical

equilibrium under the influence of three forces : Mg parallel to NV ; the reaction at V having components P along VA and Q along VG, AVG being a right angle ; and the reversed effective force $M\Omega^2\rho$ parallel to OV, where ρ has been substituted for the distance of G from the earth's axis, the ratio VG/ρ being very small. Using the notation of the preceding method, and resolving parallel to VA, we find

$$P + Mg \sin (\alpha - \theta) = M\Omega^2 \rho \cos \theta \quad . \quad . \quad . \quad (2)$$

Considering now motion relative to the centre of gravity, let $G\xi\eta\zeta$ be axes with directions fixed in space, $G\xi$ being instantaneously coincident with the normal to the plane of the meridian, drawn out from the page, $G\eta$ in the direction VG, and $G\zeta$ parallel to VA. The angular velocity of the top is compounded of the angular velocities Ω about the earth's axis and ω about VG, thus giving as components of angular velocity about $G\xi\eta\zeta$

$$0, \quad \omega + \Omega \cos \theta, \quad \Omega \sin \theta ;$$

and for components of angular momentum

$$0, \quad C(\omega + \Omega \cos \theta), \quad A\Omega \sin \theta.$$

Let GH be the angular momentum vector, and HD perpendicular to GD, a parallel to the earth's axis. Then the components of the velocity of H relative to $G\xi\eta\zeta$ are

$$-\Omega . \text{DH}, \quad 0, \quad 0,$$

and these are identical with the moments of forces about these axes, viz. $-Pa$, 0, 0.

Thus

$$-Pa = -\Omega . \text{DH},$$

or since

$$\text{DH} = C \sin \theta(\omega + \Omega \cos \theta) - A\Omega \sin \theta \cos \theta,$$

and Ω^2 is small,

$$Pa = C\omega\Omega \sin \theta. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Eliminating P between (2) and (3),

$$C\omega\Omega \sin \theta + Mga \sin (\alpha - \theta) = M\Omega^2\rho a \cos \theta,$$

which is the relation (1) obtained by the analytical method, and from which the same result follows as before.

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XLV. *Electric Moment and Molecular Structure. By* CHARLES P. SMYTH, *Ph.D., Department of Chemistry, Princeton University* *.

A PREVIOUS paper † has described a method for the calculation of the electric moment of the molecule of a substance from experimental data. The present paper considers the relation between the moments calculated for a number of substances and the structures of the systems of electrons and positive nuclei which constitute the molecules of these substances. In order to make possible the consideration of the effect of each electron, it is assumed that this effect is equivalent to that which would result if the electron were located at some fixed point. The locations of these points with reference to the positive nuclei determine the electric moment of the molecule. Since these points will be spoken of as if they were the actual locations of the electrons, the method of considering the structure of the molecule will be similar to that employed by Lewis ‡ Langmuir §, and J. J. Thomson ‖.

The positions of the centres of gravity of the positive and negative charges in a molecule are obtained in much the same way that the centre of gravity of a system of rigid bodies is located. The space coördinates, x, y, and z, of each positive charge are determined with reference to a conveniently located set of axes. If $\bar{x}$, $\bar{y}$, and $\bar{z}$ are the coördinates of the centre of gravity of the positive charges, e the value of the electronic charge $= 4 \cdot 774 \times 10^{-10}$, and E the sum of all the positive charges in the molecule, then $\Sigma e x = E\bar{x}$, $\Sigma e y = E\bar{y}$, and $\Sigma e z = E\bar{z}$. The centre of gravity of the negative charges may be located by means of an analogous set of equations:

$$\Sigma e x' = E\bar{x}', \quad \Sigma e y' = E\bar{y}', \quad \Sigma e z' = E\bar{z}'.$$

The moment, μ, of the electric doublet thus located in the molecule is determined from its components,

$$\mu_x = E(\bar{x} - \bar{x}'), \quad \mu_y = E(\bar{y} - \bar{y}'), \quad \text{and} \quad \mu_z = E(\bar{z} - \bar{z}'),$$

which give

$$\mu = E \sqrt{(\bar{x} - \bar{x}')^2 + (\bar{y} - \bar{y}')^2 + (\bar{z} - \bar{z}')^2}.$$

* Communicated by the Author.
† C. P. Smyth, Phil. Mag. xlv. p. 849 (1923).
‡ G. N. Lewis, Journ. Am. Chem. Soc. xxxviii. p. 762 (1916).
§ I. Langmuir, Journ. Am. Chem. Soc. xli. p. 868 (1919).
‖ J. J. Thomson, Phil. Mag. xli. p. 510 (1921).

The determination of the position of the centre of gravity of the electrons in a molecule is simplified by the justifiable assumption that the centre of gravity of the inner electrons of each atom is located in the nucleus of the atom and is never displaced from this position, only the electrons in the outer layer being displaced by external forces[*]. The application of this method of calculation to the hydrogen chloride molecule leads to the conclusion that the molecule may be regarded as an electric doublet, the axis of which is the line joining the two nuclei, and the moment of which is the product of one charge by the distance apart of the nuclei. From the infra-red absorption spectrum of hydrogen chloride[†] the internuclear distance is calculated as $1·265 \times 10^{-8}$ cm. This gives for the moment of the HCl molecule, $\mu = 4·774 \times 10^{-10} \times 1·265 \times 10^{-8} = 6·039 \times 10^{-18}$, as compared with the value $2·15 \times 10^{-18}$ obtained from the temperature variation of the dielectric constant of hydrogen chloride[‡].

In this calculation of the moment from the internuclear distance, no account has been taken of the displacement of the outer electrons from their symmetrical locations by the attraction of the hydrogen nucleus. The force f necessary to produce unit displacement of an electron in a molecule may be calculated from the equation[§]

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi N e^2}{3f},$$

in which ϵ is the dielectric constant of the substance, N is the number of electrons in unit volume which suffer displacement, and e is the electronic charge. This equation is derived on the assumption that an electric doublet may be induced in the molecule by the external field, but that the molecule possesses no permanent doublet. The dielectric constant may then be taken as approximately equal to the square of the refractive index of the substance, provided this is taken for a spectral region which is sufficiently far removed from an absorption band. When the molecule possesses a permanent doublet, the true dielectric constant of the substance cannot be used in the equation, but the contribution of the induced doublet, which may be calculated as before from the square of the refractive index, may be

* J. J. Thomson, *loc. cit.*; M. Born and H. Kornfeld, *Phys. Zeits.* xxiv. p. 121 (1923).
  † H. M. Randall, Journ. Opt. Soc. Am. vii. p. 45 (1923).
  ‡ H. Falkenhagen, *Phys. Zeits.* xxiii. p. 87 (1922).
  § N. R. Campbell, ' Modern Electrical Theory,' p. 34.

employed without introducing great error. N is obtained
by multiplying the number of electrons displaced in one
molecule—eight in the case of hydrogen chloride—by
$2 \cdot 705 \times 10^{19}$, the number of molecules in unit volume of the
gas under standard conditions, to which the results of
the measurement are reduced.

In the equation which has been given it is assumed that,
when an electron is displaced, it is acted upon by a restoring
force which is proportional to the displacement, and is there-
fore equal to fx, where x is the displacement. If the positive
charge of the hydrogen nucleus in the HCl molecule attracts
an electron according to the inverse square law, it will exert
a displacing force upon the electron equal to $\dfrac{e^2}{d^2}$, where d is
the distance apart of the two charges. Each of the outer
electrons will be displaced toward the hydrogen nucleus,
and, in order that there may be equilibrium in the new
positions, the following relation must hold for each electron :

$$fx = \frac{e^2}{d^2}.$$

In the HCl molecule the centre of gravity of the elec-
trons would be at a distance of $1 \cdot 265 \times 10^{-8}$ cm. from the
hydrogen nucleus if no distortion occurred. If one electron
at this distance from the hydrogen nucleus were displaced
a distance x toward it by the force of attraction, the distance
apart of the charges would be $(1 \cdot 265 \times 10^{-8} - x)$ cm., and
equilibrium would result when

$$fx = \frac{e^2}{(1 \cdot 265 \cdot 10^{-8} - x)^2}.$$

Since f may be calculated from the refractive index of
hydrogen chloride as $\cdot 71 \times 10^6$, the equation becomes

$$x(1 \cdot 265 \cdot 10^{-8} - x)^2 = \cdot 322 \cdot 10^{-24}.$$

There is no solution of this equation for any value of x
between 0 and $1 \cdot 265 \cdot 10^{-8}$, which indicates that there
should be no position of equilibrium between these values.
In other words, the hydrogen nucleus should draw the
electron to it. At least two of the electrons in the outer
layer of the undistorted HCl molecule must be less than
$1 \cdot 265 \cdot 10^{-8}$ cm. from the hydrogen nucleus, and should
therefore be attracted to it more readily than an electron
at the distance for which the calculation has been made.
Such an occurrence would be contrary to the generally

accepted ideas of atomic structure, and may be regarded as out of the question.

If a hydrogen nucleus could be attached to an argon atom, the resulting structure should resemble that of hydrogen chloride except for the presence of one more positive charge on the argon nucleus. From the value $f = 1.13 \times 10^6$ for argon, it may be calculated that a hydrogen nucleus at a distance of 1.265×10^{-8} cm. would displace an electron a distance of 0.169×10^{-8} cm. toward it. The displacement of eight electrons by a similar amount would approximately neutralize a moment equal to that calculated for the undistorted HCl molecule. If eight electrons in the outer shell of an atom are located at the corners of a cube, the diagonal of a face of which is 2×10^{-8} cm., and a hydrogen nucleus is located at a distance of 1.33×10^{-8} cm. from the nucleus of this atom on a line drawn from the nucleus at the centre of the cube through the mid-point of one edge, the displacement of each electron may be calculated for a given value of f. If f has the value 4.66×10^6, as calculated for the neon atom, the total effect of the displacement of the electrons is sufficient to reduce by 11·8 per cent. the moment which the structure would have if undistorted. The value of f here used is undoubtedly too large for this structure, which means that the actual decrease in moment would be considerably larger than 11·8 per cent. in a structure of this character.

We are confronted by the difficulty that the use of the inverse square law and the values of f calculated from the refractive index leads commonly to the impossible result that the positive charge should draw the nearer electrons directly to it. In using these values of f, it must be borne in mind that they are only average values, and that the values are presumably not the same for all the displaceable electrons in a polyatomic molecule. Furthermore, the restoring force might be expected to depend upon the direction of the displacement, and no account is taken of this. In a detailed treatment of the electronic structure of the molecule, Thomson has found it necessary to use a radical modification of the inverse square law, other investigators also having followed a similar course. In view of these facts, it is not surprising that the attempted calculations of the displacements of the electrons in the molecules have failed to account quantitatively for the discrepancies between the observed and the calculated moments of the molecules; but these displacements are clearly of such an order of magnitude that they may be regarded as the main

cause of the discrepancies observed. It will presently appear that there is a connexion between the value of f and the amount of discrepancy.

Although there is some uncertainty as to the accuracy of the absolute values obtained for f due to the approximate character of the equations used in the calculations, the values should represent fairly well the relative ease of displacement of electrons in different molecules. The following table shows that f varies for different substances in the manner which would be predicted :—

TABLE I.

Substance.	Molecular formula.	Number of displaceable electrons.	$f \times 10^{-6}$.
Neon	Ne	8	4·66
Argon	A	8	1·13
Krypton	Kr	8	0·75
Xenon	Xe	8	0·46
Fluorine	F_2	14	2·82
Chlorine	Cl_2	14	0·72
Bromine	Br_2	14	0·49
Iodine	I_2	14	0·29
Hydrogen chloride	HCl	8	0·71
Hydrogen bromide	HBr	8	0·55
Hydrogen iodide	HI	8	0·35
Methane	CH_4	8	0·71
Ammonia	NH_3	8	0·84
Water	H_2O	8	1·24
Hydrogen sulphide	H_2S	8	0·51
Oxygen	O_2	12	1·73
Sulphur dioxide	SO_2	18	1·07

For the rare gases and the halogens, f decreases with increase in atomic weight, which is accompanied by increase in radius—that is, the electrons are more easily displaced the greater their distance from the positive nucleus. This effect appears to be analogous to the electromotive behaviour of the alkali and alkaline earth metals, which show increasing electrode potential as the size of the atom increases, making greater the distance of the outer electrons from the positive nucleus, and thereby increasing the ease with which these electrons leave the atom. If the values of f for the rare gases, the halogens, or the hydrogen halides are plotted as ordinates against the atomic or molecular weights as abscissæ, smooth curves are obtained which fall rapidly at the beginning, thereby calling to mind the rapid rise in this region of the atomic volume curves for the rare gases, the halogens, and the alkali metals. The agreement between

the values of f for the outer electrons of the halogen mole-
cules and those for the electrons in the octets of the
hydrogen halides would seem to offer evidence that the
method of calculation employed involves no serious errors.
The electrons in the halogen atoms are somewhat more
easily displaced than are those in the corresponding rare
gas atoms, which might be expected in view of the smaller
nuclear charge of the halogens ; but the situation is com-
plicated by the fact that one pair of electrons is shared in
both the halogen and the hydrogen halide molecules. The
same is true in the case of the water, ammonia, and methane
molecules, in which the increasing ease of displacement of
the electrons may be due not only to the decreasing nuclear
charge, but in part also to the increased number of shared
pairs. Unfortunately, data are not available upon hydrogen
fluoride.

If there were eighteen displaceable electrons in the krypton
and xenon atoms and seventeen in the bromine and iodine
atoms, as necessitated by Langmuir's theory of the structure
of the heavy atoms, there would be a sharp increase in f on
going from argon to krypton and from chlorine to bromine,
followed by a decrease on going to the last member of each
series. As there appears to be no explanation for such
behaviour, and as there is good reason to expect the uniform
decrease obtained when the number of displaceable electrons
in the atom is assumed to be eight, this appears to give
evidence in favour of a maximum number of eight electrons
in the outer layer of the atom, which is in accord with the
theories of Bohr and Thomson and with the modification of
the Langmuir theory proposed by Bury [*].

The structure of the water molecule proposed by Langmuir
is a cubical arrangement of the electron octet formed by the
sharing of the single electrons of the two hydrogen atoms
with the six electrons in the outer shell of the oxygen atom,
the two hydrogen nuclei being held at the centres of
diagonally opposite edges of the cube. This symmetrical
arrangement of the hydrogen nuclei fails to account for the
pronounced dipolar character of the water molecule, and to
explain this, Cuy [†] uses the tetrahedral arrangement of the
octet proposed by Lewis. The location of the two hydrogen
nuclei at apices of a tetrahedron produces an unsymmetrical
molecule which should be dipolar. Thomson obtains the
necessary lack of symmetry by assuming that the electrons

[*] C. R. Bury, Journ. Am. Chem. Soc. xliii. p. 1602 (1921).
[†] E. J. Cuy, *Zeits. f. Elektrochem.* xxvii. p. 371 (1921).

lie at the corners of a structure made by twisting one face of a cube through an angle of 45° without changing its plane.

If Langmuir's theory requires that the two hydrogen nuclei be attached always to diagonally opposite edges of the cube in the water molecule, thus giving a structure which would have no moment, the fact that the experimentally determined value of the moment of the water molecule is 1.87×10^{-18} * shows that the cubical structure is impossible in this case, and, by analogy, it becomes highly improbable in the case of the other light atoms, such as carbon, nitrogen, fluorine, and neon. Similarly, Langmuir's theory applied to hydrogen sulphide leads to a symmetrical structure analogous to that of the water molecule and having no moment. The value of the moment, 1.02×10^{-18}, calculated from experimental data † shows this to be impossible, and therefore argues against the cubical structure not only for sulphur, but also for the elements standing near it in the periodic system.

Although Langmuir assumed that the hydrogen nuclei are located only on diagonally opposite edges of a cube, it appears not impossible that other arrangements of these nuclei may exist. The location of the two nuclei on opposite edges of one face would give a molecule strongly dipolar in character, and their location on non-adjacent edges of two adjacent faces would give a molecule somewhat less strongly dipolar in character. If distortion of the cube is disregarded, it may be calculated by the method already described that the electric moment of a molecule with the hydrogen nuclei attached to diagonally opposite edges is 0, the moment of the molecule with the nuclei on opposite edges of the same face is 1.41 ep, where e is the electronic charge and p is the distance of each hydrogen nucleus from the oxygen nucleus, and the moment of the molecule with the nuclei on non-adjacent edges of two adjacent faces is ep. If water consisted of a mixture of these three different types of molecules, its pronounced dipolar character would be accounted for.

If ammonia had a cubical structure and the hydrogen nuclei were attached symmetrically to edges of three different faces of the cube and in no case to two edges of the same face, the molecule would have practically zero moment. The value for the electric moment of the ammonia molecule

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* M. Jona, *Phys. Zeits.* xx. p. 14 (1919).
† C. P. Smyth, *loc. cit.*

calculated by Jona from experimental data is 1.53×10^{-18}. It might therefore be assumed, as in the case of the water molecule, that some at least of the ammonia molecules have an unsymmetrical structure in which two hydrogen nuclei are attached to opposite edges of one face of the cube. Such a structure, if there were no distortion, should have a moment equal to ep, where e and p have the same significance as in the case of the water molecule. The pronounced dipolar character of the ammonia molecule would thus be accounted for.

It is thus evident that if the molecular structures of water and ammonia are cubical, they cannot all be symmetrical. Some at least must be unsymmetrical in order to produce the electric moments which have been observed, and because of the large decrease in moment produced by displacement of the electrons in the unsymmetrical molecules it can readily be shown that these molecules would have to constitute a large fraction of the mixture in order to give an average moment as large as that observed. On the other hand, it is only reasonable to suppose that, because of the mutual repulsion of the hydrogen nuclei, the majority of the molecules would tend to be symmetrical and without moment. As a sufficiently large proportion of unsymmetrical molecules appears improbable in view of the tendency toward the formation of the symmetrical molecules, the cubical structure appears improbable.

The situation is much simpler if it is assumed that the electrons act as if located in pairs at the corners of a regular tetrahedron. An attempt was made to use the values for the principal moments of inertia of the water molecule calculated by Eucken * from the infra-red absorption spectrum to distinguish between the cubical and the tetrahedral structures for this molecule. Although the three principal moments of inertia calculated for the water molecule show that water cannot consist entirely of symmetrical cubical molecules and point toward the tetrahedral structure, they do not preclude the possibility of the existence of a mixture of symmetrical and unsymmetrical cubical molecules. It appears that the crystal structures of certain solids as revealed by X-rays give evidence in favour of a tetrahedral atomic structure †. The twisted cube proposed by Thomson gives an unsymmetrical structure which our present

* Eucken, A., *Jahrbuch d. Radioaktivität u. Electronik.* xvi. p. 408 (1919–1920).

† M. L. Huggins, Journ. Phys. Chem. xxvi. p. 601 (1922); *cf.* R. G. Dickinson, Journ. Am. Chem. Soc. xlv. p. 958 (1923).

knowledge of electric moments does not serve to distinguish definitely from the tetrahedral structure. In view of the improbability of the cubical structure for the molecules which have been considered and the simplicity of the treatment required for the tetrahedral structure, this latter will generally be used in calculating the moments of molecules in the following paragraphs.

In order to test the value of the electric moment as an indication of the molecular structure, it is of interest to compare the observed and calculated values for the moments of molecules of related substances. It has been calculated * that the volumes of the carbon, nitrogen, and oxygen octets in methane, ammonia, and water respectively are practically identical, and that each hydrogen nucleus occupies approximately the same volume in all these molecules. It thus appears that the distance, p, of a hydrogen nucleus from the nucleus of the octet is approximately the same for the three different substances. If $p = 1.0 \times 10^{-8}$ cm., the values calculated for the moments on the assumption of a tetrahedral structure are $1.155\ ep = 5.51 \times 10^{-18}$ for water, $ep = 4.77 \times 10^{-18}$ for ammonia, and 0 for methane; while the observed values are 1.87×10^{-18}, 1.53×10^{-18}, and a value less than 0.048×10^{-18} † respectively. The agreement between the observed and the calculated values for methane is satisfactory, and the discrepancies for the other two substances are of the same order of magnitude as that found in the case of hydrogen chloride. In the methane molecule the four pairs of electrons attracted by the hydrogen nuclei must suffer equal displacements so that the symmetry of the molecule is not altered and the moment remains zero. The ratio between the calculated values of water and ammonia is 1.155 and that between the observed values is 1.28, indicating that distortion of the electron positions has a slightly greater effect in reducing the moment of the ammonia molecule than it has in the case of the water molecule. This agrees with the fact that f for ammonia is 0.84×10^6, while f for water is 1.24×10^6, showing greater ease of displacement for the electrons in the ammonia molecule.

Hydrogen sulphide, presumably, has a structure analogous to that of water, and should therefore, if there were no distortion, have a moment equal to $1.155\ ep$, or 6.89×10^{-18}, where p is taken equal to 1.25×10^{-8} cm. as compared with

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* R. N. Pease, Journ. Am. Chem. Soc. xliii. p. 491 (1921).
† H. Riegger, *Ann. d. Phys.* lix. p. 753 (1919).

1.0×10^{-8} in the case of water *. However, instead of being larger than the moment of the water molecule as this would seem to indicate, the value calculated from the experimental data is 1.02×10^{-18} as compared with 1.87×10^{-18} for water. This seeming contradiction is explained by the fact that f for hydrogen sulphide is 0.51×10^6 as compared with 1.24×10^6 for water, showing that the electrons are much more easily displaced in hydrogen sulphide than in water, so that the displacement of the electrons makes a much greater decrease in the moment of hydrogen sulphide than it does in that of water, with the result that the moment of hydrogen sulphide is actually the smaller of the two.

The sulphur dioxide molecule was supposed by Langmuir to consist of a cubical sulphur atom sharing a face with one oxygen atom and an edge with the other oxygen atom. This structure may be represented by the formula $O = S^{-O}$, in which each line represents a pair of electrons shared between two atoms. If we assume, as approximate dimensions for the atoms in the molecule, 1.25×10^{-8} cm. for the radius of the sulphur and 1.0×10^{-8} cm. for the radius of the oxygen, the moment of this structure may be calculated as about 8.8×10^{-18}, considerably larger than the calculated value, 5.51×10^{-18}, for the water molecule; while the values observed, 1.76×10^{-48} by Jona and 1.87×10^{-18} by Falkenhagen, are approximately the same as that found by Jona for water. The ease of displacement of the electrons in the sulphur octet accounts for the great decrease in the moment of sulphur dioxide. The significance of the value of f, 1.07×10^6, for the outer eighteen electrons of the sulphur dioxide molecule is diminished by the rather complicated distribution of these electrons between the sulphur and the oxygen atoms, and cannot be greatly emphasized ; but it is apparent that the value of f for sulphur dioxide stands between those for water and hydrogen sulphide, as is also the case with the relative decrease in the moment due to displacement of the electrons. From viscosity measurements, Rankine and Smith † have calculated the mean area for molecular collisions of the sulphur dioxide molecule as 0.94×10^{-15} cm.², and have further calculated that a molecule of the structure $O = S^{-O}$ would have an area

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* The values used for p in this paper are approximations based upon atomic dimensions as determined from moments of inertia, X-ray measurements, and the kinetic theory of gases.

† A. O. Rankine and C. J. Smith, Proc. Phys. Soc. London, xxxv. p. 33 (1922).

1.08×10^{-15} cm.^{2}; while, if the molecule had a ring

structure, $S\Big\langle{\substack{O \\ | \\ O}}$, the area would be 0.99×10^{-15} cm.^{2}, the

conclusion being that the latter is the more probable structure. The electric moment calculated for this structure is practically zero, while that calculated for the first structure is, as has been shown, in accord with the experimental facts. It seems impossible that a structure which would have practically zero moment can be correct for the molecule of a substance which has one of the largest moments yet observed experimentally. Cubical structures have been employed in these calculations for the sulphur dioxide molecule, but the assumption of tetrahedral structures would lead to essentially the same results.

Tetrahedral structures may be employed in the calculation of the moments of the molecules of alcohols and ethers. It is found that the value of the moment depends upon the distances of the hydrogen nuclei from the oxygen and the carbon nuclei. If these distances are a and b respectively, the moment of methyl alcohol may be calculated as

$$\mu = e \sqrt{(.943\,a)^2 + (.999\,b - .333\,a)^2}.$$

It was indicated that the distance, p, of the hydrogen nuclei from the nuclei of the octets was approximately the same in the methane, ammonia, and water molecules. It might be argued from this that a would equal b, and that a and b would differ little from p. If $a = b = p$, $\mu = 1.155\,ep$, which is the calculated value of the moment of the water molecule. The value of the moment calculated for ethyl alcohol is identical with that for methyl alcohol, and consideration of the geometrical structures assumed for these compounds reveals the fact that, if distortion is neglected, an alkyl group may be substituted for a hydrogen without affecting the moment of the molecule, which means that not only the acyclic saturated alcohols, but also the ethers, should all have the same moment as water. It would appear that the more complex structure attached to the oxygen in an alcohol molecule might give greater opportunity for decrease in the moment by electronic displacement than that occurring in the water, while the decrease in an ether molecule might be somewhat greater than that in an alcohol molecule.

The comparison of calculated and observed values is complicated in the case of the alcohols by molecular association, which makes difficult the calculation of the true value of the

moment from data upon the substance in the liquid condition. From values of the dielectric constant of methyl alcohol vapour at various temperatures, Jona calculated the moment of the molecule to be $1·61 \times 10^{-18}$ as compared with $1·87 \times 10^{-18}$ obtained for water in a similar manner. In a previous paper already referred to, the writer has used a different method to calculate the moment of methyl alcohol from Jona's data, obtaining values which, although varying slightly with temperature, indicate a moment of about $1·78 \times 10^{-18}$. The same method of calculation applied to the values of the dielectric constants obtained by Abegg and Seitz [*] gives a value of $1·70 \times 10^{-18}$ for the ethyl alcohol molecule in the liquid at $20°$ and $1·71 \times 10^{-18}$ for the propyl alcohol molecule at the same temperature. These values are, presumably, somewhat low because of molecular association, but should indicate approximately the magnitudes of the moments of these molecules. The moment of the ethyl ether molecule was calculated by Isnardi and Gans [†] from dielectric constant data on the liquid as $1·435 \times 10^{-18}$, and the calculations made by the writer from their data and from the data of Bädeker [‡] on ether vapour agree well with this figure. Rather limited data obtained by Bädeker on the dielectric constant of gaseous methyl ether make possible a rough calculation of the moment of this molecule as about $1·3 \times 10^{-18}$. Too much significance cannot, however, be attached to this figure. It is apparent that the moments of the alcohol and ether molecules which have been investigated are close to the moment of water, thus agreeing with the conclusions arrived at from considerations of structure.

The moments of the chlorine substitution products of methane may be calculated, the displacement of the electrons being neglected. p is the distance of the hydrogen nuclei from the carbon nucleus, and r and c the distances from the nuclei to the outermost electrons in the chlorine and carbon atoms respectively. The moment of the methane molecule is, as has been shown, practically zero, and the moment calculated for the carbon tetrachloride molecule is also zero, while the values obtained for methyl chloride, methylene . chloride, and chloroform are, respectively, $e(r+p-c)$, $1·155\ e(r+p-c)$, and $e(r+p-c)$. The results indicate that, if there were no displacement of the electrons, methyl chloride and chloroform would have moments not

[*] R. Abegg and W. Seitz, *Zeits. f. Phys. Chem.* xxix. p. 242 (1899).

[†] H. Isnardi and R. Gans, *Phys. Zeits.* xxii. p. 230 (1921).

[‡] K. Bädeker, *Zeits. Phys. Chem.* xxxvi. p. 304 (1901).

far from that of hydrogen chloride. However, the more
complicated structures of the methyl chloride and chloroform
molecules may give greater opportunity for the decrease of the
moment by displacement of electrons, so that the moments
observed for these molecules might be expected to be some-
what lower than the value 2.15×10^{-18} observed for hydrogen
chloride. Unfortunately, the necessary experimental data
are not available for the calculation of the moment of
methyl chloride, but the moment of chlorobenzene has been
calculated by the writer in the paper already referred to as
1.42×10^{-18}, and, on account of the symmetry of the benzene
structure *, the moment of the C_6H_5Cl molecule should not
differ greatly from that of the CH_3Cl molecule. The moment
of methylene chloride was calculated from data given in
Landolt-Börnstein (fourth edition) as 1.65×10^{-18}, a value
which, because of the limited range of the data, must be
regarded as only approximate, in spite of the fact that its
ratio to the value of the moment of chlorobenzene is very
close to that indicated by structural considerations. The
value obtained by Isnardi for the moment of the chloroform
molecule is 1.26×10^{-18}, while Lertes † found 1.35×10^{-18}
for the same quantity. The mean, 1.31×10^{-18}, is in fair
agreement with the value, 1.42×10^{-18}, for chlorobenzene.
From Isnardi's data on the dielectric constant of carbon
tetrachloride, the moment may be calculated by the writer's
method as 0.39×10^{-18} at $0°$ and 0.48×10^{-18} at $62°$. The
value obtained is small, but not as small as might be expected
in view of the apparent symmetry of the carbon tetrachloride
molecule. It is not certain that the equations used in cal-
culating these values give great accuracy for small values of
the moment. It appears, however, that the molecules of this
series of compounds have electric moments of the approximate
magnitude predicted on the basis of structure.

It has been stated that the moment of the chlorobenzene
molecule is 1.42×10^{-18}. If there were no displacement of
the electrons, the bromobenzene molecule should have a
moment which would be to the moment of chlorobenzene
approximately as the radius of the bromine atom is to that
of the chlorine atom. However, f for hydrogen chloride
is 0.71×10^6, while f for hydrogen bromide is 0.55, the
quantities being very similar for the Cl_2 and Br_2 molecules
respectively. The displacement of the outer electrons will,

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* Isnardi's (*Zeits. f. Phys.* ix. p. 152, 1922) data on the dielectric
constant of benzene indicate that the moment of the molecule is
negligible.

† P. Lertes, *Zeits. f. Phys.* vi. p. 257 (1921).

therefore, be greater in bromobenzene than in chlorobenzene, and the resulting decrease in moment will be greater. The value of the moment obtained by the writer from the data of Lertes upon the dielectric constant of bromobenzene is 1.39×10^{-18}, showing that the greater ease of displacement of the electrons decreases the moment to about the same value as that observed for chlorobenzene. This effect is analogous to the great decrease in the moment of hydrogen sulphide as compared with that of water, but the effect is much less marked here because the difference between the values of f for chlorobenzene and bromobenzene is much less than the difference in the case of water and hydrogen sulphide.

There are many gaps and undoubtedly many errors in the data which have been considered, and the nature of the problem renders a precise treatment impossible in the present state of our knowledge ; but the approximate agreement obtained between the magnitudes of electric moments calculated from molecular structures and those calculated from experimental data shows that the value of the electric moment of a molecule may be taken as an indication of its structure, and, in so far as the spatial arrangement of the atoms in a molecule is dependent upon the electronic structure of the atoms, the value of the moment of the molecule may give evidence of this electronic structure. A method is thus provided for obtaining evidence as to the arrangement of the atoms in the molecule of a substance.

Summary.

A method has been described for the calculation of the electric moment of a molecule by calculating the location of the centres of gravity of the positive and negative charges in the molecule. The force necessary to produce unit displacement of an electron in the outer layer of a molecule has been calculated from the refractive indices of a number of substances in the gaseous state. By the use of this quantity and the application of the inverse square law to the attraction between positive and negative charges within the molecule, it has been shown that, although the inverse square law is not obeyed with any exactitude, the electrons suffer displacements from positions of symmetry sufficient to account for the difference between the values of the electric

moment calculated from the theoretical molecular structure
and those calculated from experimental data.

It has been further shown that (1) the force binding the
outer electrons in an atom varies in such a way among
different elements as to point to a maximum number of
eight electrons in the outer shell of the atom, thus agreeing
with the theories of Bohr, Thomson, and Bury, but differing
from that of Langmuir ; (2) the tetrahedral arrangement of
electrons is more probable than the cubical in H_2O, H_2S,
NH_3, and the closely-related molecules ; (3) the ring

structure $S\!\!\begin{array}{c}\diagup O\\ |\\ \diagdown O\end{array}$ for sulphur dioxide is much less probable

than the structure $O = S^{-O}$; (4) the observed moments of
the alcohols, ethers, and chlorine substitution products
of methane are in accord with the values indicated by
their electronic structures.

XLVI. *A Note on the Thermodynamics of Thermionic Emission. By* C. DAVISSON, *Ph.D.*[*]

IN applying the principles of thermodynamics to the
thermionic properties of hot bodies, it is customary to
consider the reversible changes possible in a system com-
prising a hot body in equilibrium with an atmosphere of
electrons inside an enclosure (cylinder and piston) whose
walls are impervious to electrons. This system differs in one
important respect from the similar system of an enclosure
containing an ordinary vapour in equilibrium with a con-
densed phase. The electrons being charged—or being
charges—the establishment of the electron atmosphere
within the enclosure is accompanied by the establishment of
an electric field, and the system comes to equilibrium with
the gaseous electrons distributed non-uniformly through the
free space. This introduces a complication which is not
present in the case of an ordinary saturated vapour. It is
no longer permissible, in general, to write down a constant
n as the number of particles per unit volume, nkT as the
pressure against the walls of the enclosure, or $n\Delta r$ as the
increase in the number of gaseous particles in the system
during an isothermal expansion Δv.

The usual procedure in treating the problem has been
to avoid these difficulties by assuming that the temperature

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[*] Communicated by the Author.

of the system is kept so low during the reversible changes that no very great number of electrons is present in the gaseous state *. The intensities of the electric field approach zero as the space-charge is reduced, assuming the net charge of the system zero, and at sufficiently low temperatures the gaseous electrons will be almost uniformly distributed. It is assumed in the simple argument that all changes take place at temperatures for which the variations in electron density may be disregarded. With this limitation the problem becomes exactly that of an ordinary saturated vapour, and one arrives at the conclusion that the pressure of the vapour (molecular or electronic) will be given by

$$p = A T \epsilon^{\int \frac{\omega d T}{k T^2}}, \quad \ldots \quad \ldots \quad (1)$$

where A is a constant, ω the work required to transfer a single particle from the condensed to the gaseous state, and k is Boltzmann's gas constant. This result is combined in the thermionic problem with a theorem of the kinetic theory to give

$$i = A' T^{1/2} \epsilon^{\int \frac{\omega d T}{k T^2}} \quad \ldots \quad \ldots \quad (2)$$

as the relation between T and i, the current density of emission.

Strictly speaking, one should carry over into the conclusion in the electrical problem the temperature restriction used in the argument; the emission should be given by equation (2), provided T is not greater than that fixed as a permissible maximum in the argument. While there is not much question as to the correctness of the usual extrapolation to higher temperatures, it will perhaps put the deduction on a more satisfactory basis to present it in a form in which the temperature restriction is entirely avoided.

Let us imagine a system of two plane parallel surfaces: one on the left that emits electrons thermionically into the region between the two surfaces, and one on the right that is a perfect reflector of electrons and is non-emitting. If the system is uncharged when cold, then when raised to a high temperature an atmosphere of electrons is built up between the two surfaces, and the emitting surface is left with a positive charge equal in magnitude to the negative charge of the electron atmosphere. The system is a charged condenser, and in considering the changes that are possible in the

* O. W. Richardson, 'Emission of Electrons from Hot Bodies,' Chap. II.

system it will be necessary to take the energy of this charged condenser into account. The total charge of the electron gas per unit area of the emitting surface will be represented by E, and the total electrostatic energy per unit area by W.

We may imagine that the emitting surface coincides with the $x=0$ plane of a system of three rectangular coordinates. The reflecting surface then coincides with the $x=X$ plane, where X is the distance between the surfaces.

The charge per unit area of the system to the right of a plane x, $(0 < x < X)$, is integral σdx from x to X, where σ represents charge density, and the charge per unit area to the left of this plane, including the charge on the emitting surface, is equal in magnitude but opposite in sign. The electric intensity at x is therefore

$$\frac{dV}{dx} = 4\pi \int_x^X \sigma dx. \quad \cdots \quad (3)$$

At the reflecting surface the intensity is zero, so that the only force acting on this surface is that due to the gas-pressure of the electron at $x=X$.

We suppose the system capable of reversible transformation in T and X. It is required, therefore, on thermodynamical principles to satisfy Clausius' relation, which for present requirements may be written $\partial p/\partial T = \lambda/T$, where p is the pressure against the reflecting surface and λ is the latent heat of isothermal expansion per unit area of the system. To evaluate λ we have that during an isothermal expansion ΔX the number of gaseous electrons per unit area of the system is increased by $(\Delta X/e)\partial E/\partial X$, where e is the charge of one electron, and that this multiplied by ω is the quantity of heat absorbed by the transfer of these electrons from the metal to the electron atmosphere. A quantity of heat $(\partial W/\partial X)\Delta X$ is absorbed in increasing the electrostatic energy of the system, and a quantity $p\Delta X$ is absorbed by the system in doing work against external forces. Assuming that heat is absorbed in no other way, we have that the quantity absorbed per unit area of the system per unit change in X is $(\omega/e)\partial E/\partial X + \partial W/\partial X + p = \lambda$, and Clausius' equation becomes

$$\frac{\partial p}{\partial T} = \frac{1}{T}\left[\frac{\omega}{e}\frac{\partial E}{\partial X} + \frac{\partial W}{\partial X} + p\right]. \quad \cdots \quad (4)$$

Since the electrons between the two surfaces are in a state of thermal equilibrium, we have by Boltzmann's relation

$\log \sigma + \mathrm{V}e/k\mathrm{T} = \text{const.}$, or $d\mathrm{V}/dx = -(k\mathrm{T}/\sigma e)d\sigma/dx$. Combining this with equation (3), we find that σ satisfies the equation

$$\frac{d\sigma}{d\mathrm{T}} = -\frac{4\pi e}{k\mathrm{T}}\sigma \int_x^{\mathrm{X}} \sigma dx.$$

The solution of this equation, supplied to me by Dr. T. C. Fry of this laboratory, is

$$\sigma = \sigma_1 \sec^2 \left[\frac{2\pi e\sigma_1}{k\mathrm{T}}\right]^{1/2} (\mathrm{X} - x), \quad \ldots \quad (5)$$

where σ_1 is a constant.

The same distribution law has been given in somewhat different form by v. Laue [*], and Schottky [†] has deduced the law of distribution of potential for the same case. Equation (5) may be readily derived from either of these results.

At $x = \mathrm{X}$, $\sigma = \sigma_1$, so that σ_1 represents the charge density at the reflecting surface, and the pressure against this surface is $p = \sigma_1 k\mathrm{T}/e$. Writing σ_0 for the charge density at the emitting surface,

$$\sigma_0 = \sigma_1 \sec^2 \mu\mathrm{X}, \quad \ldots \quad \ldots \quad (6)$$

where $\mu^2 = 2\pi e\sigma_1/k\mathrm{T}$.

The total space-charge per unit area of the system is

$$\mathrm{E} = \sigma_1 \int_0^{\mathrm{X}} \sec^2 \mu(\mathrm{X} - x)\, dx$$
$$= (\sigma_1/\mu)\tan \mu\mathrm{X}.$$

Or, combining this with (6),

$$\mathrm{E} = \sigma_1^{1/2}(\sigma_0 - \sigma_1)^{1/2}/\mu = \left[k\mathrm{T}(\sigma_0 - \sigma_1)/2\pi e\right]^{1/2}. \quad . \quad (7)$$

The density of electrostatic energy at x is

$$\frac{1}{8\pi}\left(\frac{d\mathrm{V}}{dx}\right)^2 = 2\pi\left(\int_x^{\mathrm{X}} \sigma dx\right)^2 = (2\mu\sigma_1^2/\mu^2)\tan^2 \mu(\mathrm{X} - x)\ ;$$

so that

$$\mathrm{W} = \frac{2\pi\sigma_1^2}{\mu^2}\int_0^{\mathrm{X}}\tan^2 \mu(\mathrm{X} - x)dx$$
$$= (2\pi\sigma_1^2/\mu^3)\,(\tan \mu\mathrm{X} - \mu\mathrm{X}).$$

Or, combining this with (6) and (7),

$$\mathrm{W} = (2\pi\sigma_1^{3/2}/\mu^3)\left[(\sigma_0 - \sigma_1)^{1/2} - \mu\sigma_1^{1/2}\mathrm{X}\right]$$
$$= (k\mathrm{T}/e)(\mathrm{E} - \sigma_1\mathrm{X}). \quad \ldots \quad \ldots \quad (8)$$

* v. Laue, *Jahrb. der Rad. u. Elektronik*, xv. p. 205 (1918).
† Schottky, *ibid.* xii. p. 199 (1905).

We thus have expressions for p, E, and W in terms of T, X, σ_1, and σ_0. Differentiating these partially as required for substitution in (4), we find

$$\frac{\partial p}{\partial T} = \frac{k}{e}\left[\sigma_1 + T\frac{\partial \sigma_1}{\partial T}\right],$$

$$\frac{\partial E}{\partial X} = -\left[\frac{kT}{8\pi e}\right]^{1/2}\frac{\partial \sigma_1}{\partial X}\Big/(\sigma_0 - \sigma_1)^{1/2},$$

and

$$\frac{\partial W}{\partial X} = -\frac{kT}{e}\left[\sigma_1 + X\frac{\partial \sigma_1}{\partial X} + \left(\frac{kT}{8\pi e}\right)^{1/2}\frac{\partial \sigma_1}{\partial X}\Big/(\sigma_0 - \sigma_1)^{1/2}\right].$$

Substituting into (4) and collecting terms, we find that

$$-T\frac{\partial \sigma_1}{\partial T} = \left(\frac{kT}{8\pi e}\right)^{1/2}\left(1 + \frac{\omega}{kT}\right)\frac{\partial \sigma_1}{\partial X}\Big/(\sigma_0 - \sigma_1)^{1\cdot 2}$$

$$+ \left(\sigma_1 + X\frac{\partial \sigma_1}{\partial X}\right). \quad . \quad . \quad . \quad . \quad . \quad (9)$$

We next differentiate (6) partially with respect to T and X, obtaining

$$\frac{\partial \sigma_0}{\partial T} = \frac{\partial \sigma_1}{\partial T}\sec^2 \mu X + \mu X\left(\frac{\partial \sigma_1}{\partial T} - \frac{\sigma_1}{T}\right)\sec^2 \mu X \tan \mu X$$

$$= \frac{\sigma_0}{\sigma_1}\left[\frac{\partial \sigma_1}{\partial T} + \left(\frac{2\pi e}{kT}\right)^{1/2}\left(\frac{\partial \sigma_1}{\partial T} - \frac{\sigma_1}{T}\right)(\sigma_0 - \sigma_1)^{1/2}X\right]$$

and

$$\frac{\partial \sigma_0}{\partial X} = 0 = \frac{\partial \sigma_1}{\partial X}\sec^2 \mu X + \mu X\left(\frac{\partial \sigma_1}{\partial X} + \frac{2\sigma_1}{X}\right)\sec^2 \mu X \tan \mu X$$

$$= \frac{\partial \sigma_1}{\partial X} + \left(\frac{2\pi e}{kT}\right)^{1/2}\left(\frac{\partial \sigma_1}{\partial X} + \frac{2\sigma_1}{X}\right)(\sigma_0 - \sigma_1)^{1/2}X.$$

Solving these for the $\partial \sigma_1/\partial T$ and $\partial \sigma_1/\partial X$, gives

$$\frac{\partial \sigma_1}{\partial T} = \left[\frac{\sigma_1}{\sigma_0}\frac{\partial \sigma_0}{\partial T} + \left(\frac{2\pi e}{kT}\right)^{1/2}\frac{\sigma_1 X}{T}(\sigma_0 - \sigma_1)^{1/2}\right]$$

$$\div \left[1 + \left(\frac{2\pi e}{kT}\right)^{1/2}X(\sigma_0 - \sigma_1)^{1/2}\right]$$

and

$$\frac{\partial \sigma_1}{\partial X} = -\left(\frac{8\pi e}{kT}\right)^{1\cdot 2}\sigma_1(\sigma_0 - \sigma_1)^{1\cdot 2}\Big/\left[1 + \left(\frac{2\pi e}{kT}\right)^{1\cdot 2}X(\sigma_0 - \sigma_1)^{1/2}\right].$$

On substituting these into (9), the equation is found to reduce to

$$\frac{1}{\sigma_0}\frac{\partial \sigma_0}{\partial T} = \frac{\omega}{kT^2},$$

which integrates to

$$\sigma_0 = A\epsilon^{\int \frac{\omega dT}{kT^2}}.$$

From this point the deduction follows the usual lines. The number of electrons per unit volume at the emitting surface is σ_0/e, and, by the theorem of the kinetic theory already referred to, the number striking unit area of the emitting surface in unit time is

$$N = \frac{\sigma_0}{e}\left(\frac{kT}{2\pi m}\right)^{1/2},$$

where m is the mass of the electron. If the coefficient of reflexion of the surface for electrons is zero, this is also the number emitted from unit area in unit time. The current density of emission is then given by

$$i = Ne = A\left(\frac{kT}{2\pi m}\right)^{1/2}\epsilon^{\int \frac{\omega dT}{kT^2}} = A'T^{1/2}e^{\int \frac{\omega dT}{kT^2}}.$$

We thus arrive at equation (2) without introducing a temperature restriction into the argument.

Research Laboratories of the
American Telephone and Telegraph Company,
and the Western Electric Company, Inc.
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XLVII. *The Halogen Hydrides.* By HERBERT BELL, *Lecturer in Physics, Manchester University* *.

Summary.

THE absorption-band spectra in the infra-red of the halogen hydrides HF, HCl, HBr have recently been determined very carefully by several investigators. In this paper the experimental data have been analysed with the aid of the energy-formula developed by Born and Hückel. It is shown that the values of the coefficients in the formula $1/\lambda = c_0 + c_1 m + c_2 m^2 + c_3 m^3$ which embodies the experimental

results for the main band and its overtones are, within the limits of experimental error, consistent with theory. The accuracy is not sufficient, however, to decide whether the " zero-point energy " exists or not.

The significance of the constants in the formula is discussed. Their determination makes it possible to evaluate the variation with distance of the force acting on the hydrogen nucleus as it vibrates along the line joining the two nuclei. The range of vibration for one, two, and three energy quanta is calculated.

The HCl Molecule.

Spectral Data.

The infra-red absorption band of HCl at $3 \cdot 5\mu$ has recently been carefully investigated * by Colby, Meyer, and Bronk, and the wave numbers of the individual lines are found to be represented by

$$1/\lambda = 2886 \cdot 07 + 20 \cdot 60m - \cdot 301m^2 - \cdot 00206m^3, \quad . \quad (1)$$

where m has successive integral values from -19 to $+20$ excluding $m = 0$, the missing central line.

From the earlier pioneer work of Imes † on the " overtone " at $1 \cdot 76\mu$ a least square formula may be obtained :

$$1/\lambda = 5667 \cdot 0 + 20 \cdot 14m - \cdot 558m^2 - \cdot 000086m^3. \quad . \quad (2)$$

The latter constants are, however, much less accurately determined, as there are only 16 lines $m = -8$ to $m = +8$ and the isotope lines also interfere.

General.

It is well known that these and similar band spectra represent quantum jumps of the molecule from a lower energy level to a higher one as light energy is absorbed. The molecular energy is in part due to oscillations along the line of join of nuclei, and in part to a rotation about an axis perpendicular to this line.

Various approximations to the mathematical solution of such a model have been given, and we may mention in particular those of Kratzer ‡ and of Born and Hückel §. We shall use the notation and formula developed by the latter investigators.

* Astroph. Journal, lvii. (Jan. 1923).
† Astroph. Journal, l. p. 251 (1919).
‡ Sommerfeld's *Atombau u. Spektrallinien.*
§ *Physik. Zt.* xxiv. (Jan. 1923).

Let the nuclei of the molecule when not oscillating or rotating be in equilibrium at a distance r_0 from each other, and let us suppose that the force function $U(r)$ along the line of join depends on r only and has derivatives U_0', U_0'', etc., at this point. If, now, the molecule be given n radial quanta and m' rotational quanta, the energy W is, according to Born and Hückel, given by

$$W_{m'}^n = U_0 + nh\nu_0 \left(1 + \frac{(\beta+3)\gamma^2}{2\nu_0^2} m'^2\right) \\ - n^2h\delta + \tfrac{1}{2}h\gamma m'^2 - \tfrac{1}{2}h\gamma^3 m'^4/\nu_0^2, \quad . \quad (3)$$

where the following abbreviations are used :

$$2\pi\nu_0 = \sqrt{U_0''/\mu}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where μ is the reduced mass of the system and ν_0 is the frequency of small oscillations,

$$\beta = r_0 U_0'''/U_0'', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\gamma = h/4\pi^2\mu r_0^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\delta = 5\gamma/48(\beta^2 - 3r_0^2 U_0^{iv}/5U_0''). \quad . \quad . \quad (7)$$

It is here understood that n may have any positive value, but may change only by integral steps from, say, n_0 to $n + n_0$, while m' may be either positive or negative, fractional or integral, but, according to the Correspondence Principle, may change only by unit steps, if at all. An equivalent statement for m' if it changes is that it can only *increase algebraically* to $m'+1$. For if we imagine an observer looking in any direction, he will see molecules spinning both to left and right, m' positive or negative, but if he disregards all those whose angular momentum on changing does not increase in an algebraic sense, and leaves these to a second observer looking in the opposite direction who in turn disregards all others, then both observers will record only algebraic increase and will take into account all the molecules. From this point of view, negative values of m' correspond to molecules suffering an energy decrease.

Band Formulæ.

The frequency of the absorbed light is now, by Bohr's principle, given by

$$\nu = (W_{m'+1}^{n+n_0} - W_{m'}^{n_0})/h ;$$

and performing the necessary algebra we obtain

$$\nu = n\{\nu_0 - 2n_0\delta - (\beta+3)(m'+1)^2\gamma^2/2\nu_0 - n\delta\} \\ + (m'+\tfrac{1}{2})\gamma\{1 + \gamma n_0(\beta+3)/\nu_0\} - 3\gamma^3 m'^2/\nu_0^2 - 2\gamma^3 m'^3/\nu_0^2. \quad (8)$$

The central missing line must be included in this; and assuming that it corresponds to a definite small value of m', say m_0', and writing $m = m' - m_0'$, equation (8) becomes

$$\nu = cc_0 + m\gamma\{1 + \gamma(\beta+3)[n_0 + n(m_0'+1)]/\nu_0\}$$
$$+ nm^2\gamma^2\frac{(\beta+3)}{2\nu_0}\left\{1 - \frac{3\gamma(m_0'+1)}{n\nu_0(\beta+3)}\right\} - 2\gamma^3m^3/\nu_0^2, \quad . \quad (9)$$

where $cc_0 = n\{\nu_0 - 2n_0\delta + \gamma^2(\beta+3)(m_0'+1)^2/2\nu_0 - n\delta\}$
$$+ (m_0' + \tfrac{1}{2})\gamma(1 + \gamma n_0(\beta+3)/\nu_0) \quad . \quad (10)$$

is the frequency of the missing line, $(m=0)$.

[If m' does not change with n, then (8) is replaced by

$$\nu = (W_{m'}^{n+n_0} - W_{m'}^{n_0})/h$$
$$= n(\nu_0 - 2n_0\delta - n\delta) + nm'^2(\beta+3)\gamma^2/2\nu_0,$$

a band without a centre which has not as yet been observed in the infra-red, but occurs frequently in the visible.]

Now Kratzer has given a formula for successive band centres, the nth one being expressed by

$$cc_0 = n(\bar{\nu} - nx), \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where x is a small quantity and $\bar{\nu}$ is a constant. This formula has been verified in several cases as far as observational data allow. We notice that if the law holds exactly, then by (10) $m_0' + \tfrac{1}{2} = 0$, so that the missing line denotes an absence of absorption, due to reversals in the molecule from an angular momentum of a half quantum to a half quantum in the opposite direction. This idea has several attractions. It endows the molecules permanently with at least a half quantum such as was demanded by Einstein and Stern [*] in the case of H_2 for the specific heat at low temperatures. The half quantum has also been found necessary by Kratzer [†] and by Curtis [‡] for several bands in the visible. Furthermore we note that, as regards the energy of rotation, no increase is demanded for this reversal, and correspondingly no absorption of light-energy is to be expected.

Determination of Constants.

Leaving the point undecided for the present, we represent the bands in general by

$$\nu = cc_0 + cc_1m + cc_2m^2 + cc_3m^3, \quad . \quad . \quad (12)$$

* *Ann. d. Phys.* xl. p. 551 (1913).
† *Ann. d. Phys.* lxxi. p. 72 (1923).
‡ Proc. Roy. Soc. A, ciii. p. 314 (1923).

where cc_0 is given by (10)

$$cc_1 = \gamma\{1 + \gamma(\beta + 3)[n_0 + n(m' + 1)]/\nu_0\}, \quad . \quad . \quad (13)$$

$$cc_2 = n\gamma^2(\beta + 3)/2\nu_0 \left\{ 1 - \frac{3\gamma(m_0' + \frac{1}{2})}{n(\beta + 3)\nu_0} \right\}, \quad . \quad (14)$$

$$cc_3 = -2\gamma^3/\nu_0^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

A preliminary approximate verification of these formulæ is obtained at once by noting that $c_0^2 c_3/2c_1^3 = -n^2$ approximately. This is obtained by neglecting γ/ν_0 in comparison with unity, as can readily be seen to be legitimate on comparing (10), (12) ... (15) with (1). Substituting values for the fundamental from (1), we therefore have $n^2 = \frac{1}{2}(2886)^2 \times \cdot00206/(20\cdot6)^3 = \cdot98$, showing that $n = 1$.

For the overtone $n = 2$ we cannot apply this test owing to inaccuracy in the determination of c_3. By (15), in fact, the coefficient of m^3 should be the same in (2) as in (1), whereas (2) gives $\cdot000086$ against $\cdot00206$.

We easily find that approximately $\beta = -7$, for approximately

$$c_0 c_2/c_1^2 = \frac{1}{2}n^2(\beta + 3)(1 - n\delta/\nu_0) \div \{1 + 2(\beta + 3)\gamma n(m_0' + 1)/\nu_0\}$$

on neglecting squares of γ/ν_0 and taking $n_0 = 0$. Hence

$$\beta = -3 + \frac{2}{n^2} \frac{c_0 c_2}{c_1^2}\left(1 + \frac{n\delta}{\nu_0}\right)(1 + 2\gamma n(\beta + 3)(m_0' + 1)/\nu_0). \quad (16)$$

Substituting from the fundamental, we have approximately

$$\beta = -3 - 2 \times 2886 \times \cdot301/(20\cdot6)^2 = -7\cdot1,$$

while the overtone gives $\beta = -3 - \frac{2}{4}\frac{5887 \times \cdot588}{(20\cdot1)^2} = -7\cdot2$ in excellent agreement. We shall take $\beta = -7$, and proceed to compare the c_1's for the fundamental and overtone. From (1), (2), and (13) we have, on putting $n_0 = 0$, $\beta = -7\cdot1$,

$$20\cdot60c = \gamma(1 - 4\cdot1\gamma(m_0' + 1)/\nu_0),$$
$$20\cdot14c = \gamma(1 - 8\cdot2\gamma(m_0' + 1)/\nu_0),$$

giving $\qquad \gamma = 41\cdot20c - 20\cdot14c = 21\cdot0c$

and $\quad \cdot46c = 4\gamma^2(m_0' + 1)/\nu_0,$

or $\qquad m_0' + 1 = \cdot75; \ m_0' = -\cdot25$

midway between the half quantum and the value zero usually assumed. A decrease in $20\cdot14$ to $19\cdot98$ would reduce m_0' to zero. The band data, however, appear too definite for this.

Returning now to (10), we have approximately, on neglecting $(\gamma/\nu_0)^2$, with $n_0 = 0$

$$cc_0 = n(\nu_0 - n\delta) + \gamma(m_0' + \tfrac{1}{2}).$$

Substituting from (1) and (2),

$$\nu_0 - \delta = 2886 - 5 = 2881,$$

$$2\nu_0 - 4\delta = 5667 - 5 = 5662,$$

$$\text{or } \delta = 50c \; ; \; \nu_0 = 2931c.$$

A second overtone is predicted at $(n=3)$:

$$3\nu_0 - 9\delta + 5 = 8548 \; ; \; \lambda = 1\cdot198\mu.$$

Using low resolving power, Schaefer * detected this band at approximately $1\cdot190\mu$, which is perhaps in agreement within the limits of experimental error. It will be found that taking $m_0' + \tfrac{1}{2} = 0$ makes very little difference in the predicted position, $1\cdot199\mu$ instead of $1\cdot198\mu$.

The Heat Band.

Colby, Meyer, and Bronk (*loc. cit.*) have also investigated the absorption of HCl at high temperatures ($500°$ C.), and have discovered five new lines belonging to the band of unit quantum absorption by molecules already possessing one quantum due to heat agitation. Whatever value m_0 may have for the fundamental, and we have assumed it to be zero, it is $n_0 + 1$ in this case, and consequently the expected centre cc_0 is by formula (10) displaced by $2\delta = 100c$ towards longer wave-lengths, i. e., $\bar{c}_0 = 2786$. At the same time, by (13) $\bar{c}_1$ is reduced relatively to c_1 of the fundamental by the factor $1 + \gamma(\beta + 3)/\nu_0 = \cdot971$. Hence $c_1 = 20\cdot60 \times \cdot971 = 20\cdot0$. c_2 and c_3 are unaffected, so that we may predict the formula

$$1/\lambda = 2786\cdot0 - 20\cdot0 \, m - \cdot301m^2 - \cdot00206m^3. \quad (17)$$

The following table shows the agreement between the observed lines and their positions as given by this formula :—

m.	ν (calc.).	ν (obs.).	Obs.—Calc.
$-\,9$	$2563\cdot2$	$2759\cdot7$	$3\cdot5$
-10	$2558\cdot0$	$2554\cdot7$	$3\cdot3$
-11	$2532\cdot4$	$2528\cdot8$	$3\cdot6$
-12	$2506\cdot3$	$2502\cdot1$	$4\cdot2$
-13	$2479\cdot7$	$2476\cdot0$	$3\cdot7$
			$3\cdot7$

* *Zt. f. Phys.* (6) xii. p. 330.

The remaining lines are smothered by the main band which it overlaps, but in the open space of the fundamental at the missing line we might expect to uncover the heat band. The investigators in searching for grating " ghosts " found an irregularity " near the base of -1," *i. e.* > 2865. Putting $m = +5$ in the above formula, we obtain 2879. A closer fit is obtained by adding $3 \cdot 7 \text{cm.}^{-1}$ to the formula, which is equivalent to reducing 2δ by this amount, *i. e.* from $100c$ to $96 \cdot 3c$. To make this consistent with (10) and the previous calculation, m_0' requires to be $- \cdot 09$ instead of $- \cdot 24$. It may confidently be predicted that further lines in this band will be of critical value in determining the band constants.

The Oscillation Constants.

Distance between the nucleii, r_0. With $\gamma = 21 \cdot 0 \times 3 \times 10^{10}$ and $h = 6 \cdot 55 \times 10^{-27}$ we have from (6), on taking $\mu = 1 \cdot 616 \times 10^{-24}$ gm.,

$$r_0 = 1 \cdot 27 \times 10^{-8} \text{ cm.}$$

Natural frequency of small oscillations, ν_0. With $m_0' = - \cdot 24$ we have already obtained

$$\nu_0 = 2931c.$$

Indeterminateness in m_0' only slightly affects this value.

Returning to (16) with the above constants and $m_0' = - \cdot 24$, we have from the $3 \cdot 5\mu$ band $\beta = - 7 \cdot 00$, while the less accurate formula for the overtone gives $\beta = - 6 \cdot 9$; we may therefore take

$$\beta = - 7 \cdot 00.$$

The Equation of Motion.

Assuming the molecule to be oscillating without rotation so that r_0 is the equilibrium distance and $U_0' = 0$, we have

$$\mu \ddot{x} = - \frac{d}{dx} U = - U_0'' x - \tfrac{1}{2} U''' x^2 - \tfrac{1}{6} U^{iv} x^3 - \dots \quad (18)$$

or $\qquad \ddot{x} = - k_1 x - k_2 x^2 - k_3 x^3 - \dots$.

Now, the solution of this equation has been given by Hettner [*] as

$x = - \tfrac{1}{2} k_2 / k_1 A^2 + A \cos \phi t + \tfrac{1}{6} k_2 / k_1 A^2 \cos 2\phi t$
$\qquad\qquad + \tfrac{1}{16} A^3 (k_2^2 / 3 k_1^2 + k_3 / 2 k_1) \cos 3\phi t + \dots$

where $\qquad \phi = k_1^{1 \cdot 2} \left(1 - \frac{5}{12} \frac{k_2^2}{k_1^2} A^2 + \frac{3}{8} \frac{k_3}{k_1} A^2 - \dots \right).$

* *Zt. f. Phys.* i. p. 349 (1920).

On comparing coefficients of (18) and (19),

$$k_2/k_1 = U_0'''/2U_0'' = \beta/2r_0 \text{ by (5)},$$

$$k_3/k_1 = U_0^{\mathrm{iv}}/6U_0'' = \frac{5}{18r_0^2}(\beta^2 - 48\delta/5\gamma) \text{ by (7)}.$$

Equation (18) therefore becomes

$$\ddot{x}/4\pi^2\nu_0^2 = -r_0\Big\{ x/r_0 + \tfrac{1}{2}\beta(x/r_0)^2 \\ + \tfrac{1}{18}(5\beta^2 - 48\delta/\gamma)(x/r_0)^3 - \ .. \ \Big\}, \quad . \quad . \quad (20)$$

having the solution, on writing η for A/r_0,

$$x/r_0 = -\tfrac{1}{4}\beta\eta^2 + \eta\cos\phi t + \tfrac{1}{12}\beta\eta^2\cos 2\phi t \\ + \tfrac{1}{72}(\beta^2 - 6\delta/\gamma)\eta^3\cos 3\phi t - \ ..., \quad . \quad (21)$$

with
$$\phi = 2\pi\nu_0(1 - \delta/\gamma\eta^2). \quad . \quad . \quad . \quad . \quad (22)$$

To determine the constant A, we have the quantum condition

$$nh = \oint \mu\dot{x}\,dx = 2\int_0^{\mathrm{T}} \mu\dot{x}^2\,dt, \quad . \quad . \quad . \quad (23)$$

where T is the half period of oscillation, so that

$$\phi\mathrm{T} = \pi.$$

Now, from (21)

$$\dot{x}/r_0 = -\phi\eta\Big\{ \sin\phi t + \tfrac{1}{6}\beta\eta\sin 2\phi t \\ + \tfrac{1}{24}(\beta^2 - 6\delta/\gamma)\eta^2\sin 3\phi t - \ ... \Big\}$$

so that $\dot{x}^2$ involves products of the form $\sin p\phi t \sin q\phi t$ where p and q are integers. The integral of such products over a half oscillation vanishes except when $p = q$, in which case

$$\int_0^{\mathrm{T}} \sin^2 p\,\phi t\,dt = \tfrac{1}{2}\mathrm{T} = \pi/2\phi.$$

Hence, squaring $\dot{x}/r_0$ and substituting in (23), we have on integrating

$$nh/2\mu r_0^2 = \phi^2\eta^2\frac{\pi}{2\phi}\left\{ 1 + \frac{\beta^2}{36}\eta^2 + \left(\frac{\beta^2 - 6\delta/\gamma}{24}\right)^2\eta^4 - ... \right\},$$

and on substituting from (22) and (6),

$$2n\gamma = \frac{nh}{2\pi^2\mu r_0^2} = \nu_0\eta^2\left[1 - (\delta/\gamma - \beta/36)\eta^2 \\ + \left\{ (\beta/24 - \delta/4\gamma)^2 - \frac{\beta\delta}{36\gamma} \right\}\eta^4 - ... \right]$$

or

$$(\delta/\gamma - \beta/36)\eta^4 - \eta^2 + 2n\gamma/\nu_0 = \left(\frac{\beta^2}{576} + \frac{7}{144}\frac{\beta\delta}{\gamma} + \frac{\delta^2}{16\gamma^2} \right)\eta^6. \quad (24)$$

Range of Oscillation. Substituting in this equation $\delta = 50c$, $\gamma = 21 \cdot 0c$, $\beta = -7 \cdot 00$, $\nu_0 = 2931c$, and solving for η^2, we have

$$\eta^2 = (A/r_0)^2 = \cdot 0149, \cdot 0308, \cdot 0486,$$
$$A/r_0 = \cdot 122, \cdot 176, \cdot 220,$$

corresponding respectively to $n = 1, 2, 3$.

To find the range of oscillation, we substitute $\phi t = 0$ and $\phi t = \pi$ in (21) and subtract, giving

$$\text{Range}/r_0 = 2\eta\left(1 + \frac{\beta^2 - 6\delta/\gamma}{72}\eta^2\right), \quad . \quad . \quad (25)$$

or on using the values of η given above, we find that the relative half amplitudes are

$$\cdot 123, \cdot 179, \cdot 225.$$

Similarly, by adding instead of subtracting, we obtain for the relative displacement of the mean centre

$$\bar{x}/r_0 = -\beta/6\eta^2, \quad . \quad \quad . \quad . \quad . \quad (26)$$

having the respective values $\cdot 017, \cdot 036, \cdot 057$. The oscillation centre is thus displaced by an amount proportional to the energy, a result[*] given by Debye.

Fig. 1.
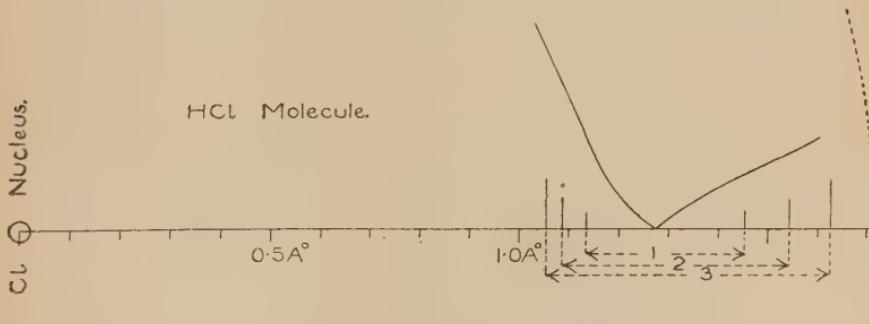
These results are represented graphically in fig. 1. The Cl nucleus is represented as at rest and a scale of Ångström units attached. The relative field of force acting on the H nucleus when displaced is shown by the curve, which is calculated from (20) and drawn so that the height represents the restoring force. It brings out clearly the steepness of the gradient on the Cl side. The range of oscillation for the fundamental band and the overtones is also indicated.

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[*] *Math. Vorlesungen an der Univ. Göttingen*, vi. p. 26.

The HF and HBr Molecules.

The band spectra for these molecules have not been nearly so well measured. From Imes's data for HF the least square formula can be derived

$$1/\lambda = 3962 \cdot 5 + 40 \cdot 34 m - \cdot 76 m^2 - \cdot 015 m^3, \quad . \quad (27)$$

and for HBr

$$1/\lambda = 2559 \cdot 2 + 16 \cdot 52 m - \cdot 23 m^2 - \cdot 002 m^3. \quad . \quad (28)$$

Using equation (16), we have approximately

$$\beta_{HF} = -6 \cdot 7 \; ; \; \beta_{HBr} = -7 \cdot 3.$$

Assuming $m_0' = - \cdot 24$ as in HCl and applying (13), we have

$$\gamma_{HF} = 41 \cdot 5 c \; ; \; \gamma_{HBr} = 17 \cdot 9 c.$$

Hence, solving (6),

$$r_{0HF} = \cdot 97 \times 10^{-8} \text{ cm.} \; ; \; r_{0HBr} = 1 \cdot 37 \times 10^{-8} \text{ cm.}$$

As regards the constant δ, which requires the exact centres of the overtones for its determination, we have only approximate values. For HF the overtone was observed by Schaefer (*loc. cit.*) at $1 \cdot 27 \mu$, *i. e.* $7 \cdot 87 \times 10^3$ cm^{-1}. For HBr, Brinsmeade and Kemble [*] obtained $1 \cdot 98 \mu$ or $5 \cdot 05 \times 10^3$ cm.$^{-1}$

With these values and applying Kratzer's formula (11), we obtain x, which is approximately δ, as

$$\delta_{HF} = (27 \pm 5) c \; ; \; \delta_{HBr} = (34 \pm 5) c.$$

Since $\delta_{HCl} = 50 c$ and the constants for HCl in other cases all lie intermediate between those of HF and HBr, we cannot regard these approximations with any confidence.

Neglecting δ and proceeding to an approximate solution of the motion, we have from (24)

$$\eta^2 = A^2/r_0{}^2 = 2n\gamma/\nu_0 = \cdot 021 \text{ for HF,}$$
$$= \cdot 0140 \text{ for HBr,}$$
$$= \cdot 0143 \text{ for HCl.}$$

The relative range of oscillation for HF is thus considerably larger than for the other two, due, of course, to the larger relative size of its quantum. The restoring force U_0'' for HF, HCl, and HBr near the position of equilibrium varies as $\mu\nu_0{}^2$ or

$$1 \cdot 84 : 1 : \cdot 80.$$

[*] Proc. Nat. Acad. Wash. vol. iii. p. 420 (1918).

The corresponding relative variation of this with distance or U_0'''/U_0'' is

$$1\cdot 33 : 1 : \cdot 98.$$

It has already been pointed out * by W. L. Bragg and the writer that the progressive increase in nuclear separation for HF, HCl, HBr is very nearly equal to the corresponding increase in size of the atomic " radius " as determined by X-ray analysis. With the tentative atomic radii which Bragg had calculated, this led to the result that the H nucleus was in all cases at the same distance ·26 angstroms from the halogen shell. Later work by Wasastjerna † has, as Professor Bragg has kindly pointed out to the writer, considerably modified these dimensions, although, of course, the X-ray nuclear distances are retained. The halogen atoms have all been increased by a constant quantity at the expense of other atoms. The radius of Cl^-, for example, has been increased from 1·05 angstroms to 1·72, its new radius being indicated in the figure by the outer circle. This value agrees closely with that given recently by Davey ‡. Examination of the scattering effects of NaCl by Bragg, James, and Bosanquet § has also shown that the effective shell of Cl^- ends between 1·6 and 1·8 angstroms. We may now therefore deduce that the H nucleus is well within the halogen shell, and is buried to the same depth for all three, HF, HCl, and HBr.

Fig. 2.
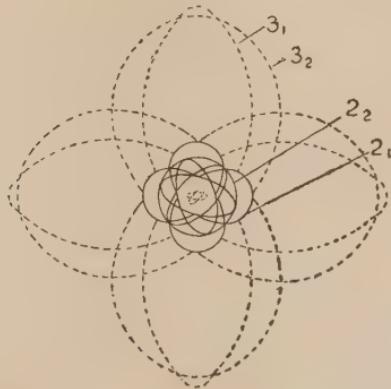
Fig. 2 represents the argon electron " economy " as given by Kramers ‖ and reproduced with his kind permission.

* 'Nature,' March 24, 1921.
† *Commentationes. Physico-Math.* I. vol. xxxviii. *Soc. Scient. Fennica.*
‡ Physical Review, vol. xxii. (Sept. 1923).
§ Phil. Mag. xliv. p. 444 (1922).
‖ *Naturwissenschaften,* 1923, p. 550.

We may take this as representing closely to scale the Cl^- atom, and identifying its outer orbits with the 1·72 angstrom sphere of fig. 1, we see that the inner neon shell has a radius of only about half an angstrom. Comparing the two figures then, we see that the oscillations of the H nucleus are always well outside the neon shell.

The author wishes to express his appreciation of the interest and encouragement shown by Professor W. L. Bragg in this work.

Physics Dept.,
University of Manchester,
Dec. 1923.

P.S.—Since writing the above, Mr. D. R. Hartree has kindly sent me the following note on the dimensions of the Cl^- ion :—

" Wasastjerna's figure of 1·72 A.U. refers rather to the *apparent* size of this ion in crystals than to the actual dimensions of the orbits. It seems probable that any value of the apparent radius of an ion, derived either from the kinetic theory ' diameter' of the atom of the neighbouring inert gas (as Wasastjerna's value is) or from the packing of monatomic ions in crystals (as is the case for Davey's value) is only an upper limit for the real radius of the ion (defined as the radius of the smallest sphere enclosing all orbits of the ion).

"An estimate of this latter quantity can be obtained by an extension of the work of which an account is given in Proc. Camb. Phil. Soc. vol. xxi. Part 6, p. 625 (1923). The value 1·22 A.U. for the radius of the Cl^- ion in this sense has been given in a recent paper [Phil. Mag. vol. xlvi. p. 1091 (1923)]; later work suggests that this value may be somewhat too low.

" The diagrams of orbits in Kramer's paper (*Naturwissenschaften*, Heft 27, p. 550) are intended to be drawn approximately to scale, though it is not stated how the dimensions of orbits were obtained. Measuring up on this diagram, the radius of the argon atom appears to be about 1·15 A.U. From ionic refractivity Wasastjerna (*loc. cit.*) deduces the figure 1·20 for the ratio of the radius of Cl^- (in the present sense) to that of A, which gives 1·38 A.U. for the radius of the Cl^- ion.

" These estimates are both rather rough, but it seems likely that the radius of Cl^- is about 1·3 A.U.; if this value is correct, and if the ion were not distorted by the presence of the H nucleus, the latter would thus be situated about on the boundary of the ion."

XLVIII. *On the Law and Mechanism of the Emission of Electrons from Hot Bodies.* By SURESH CHANDRA ROY, *M.Sc., Research Scholar in Physics, University College of Science, Calcutta* [*].

INTRODUCTION.

THE law of dependence of thermionic currents on temperature was given first by Richardson [†] on the view that these currents were due to electrons shot out owing to the vigour of their thermal motions, and he adduced experimental evidence [‡] in support of his conclusions. The deduction of his law was based on the supposition that the electrons, both outside and inside the hot body, were governed by the same laws of classical dynamics. On this supposition, he got the following expression for the thermionic current per unit area per sec. :

$$I = \int_{\left(\frac{2\phi}{m}\right)^{\frac{1}{2}}}^{\infty} ne\, x \left(\frac{m}{2\pi k T}\right)^{\frac{1}{2}} e^{-\frac{m}{2kT} x^2} dx, \quad . \quad . \quad (1)$$

where ϕ is the work done during the transference of one electron from the hot body to the outside,

m = electronic mass,

e = electronic charge,

n = number of electrons per c.c., and

k = gas constant per mol.

On treating n as constant and independent of temperature,

$$I = A_1 T^{\frac{1}{2}} . e^{-\frac{\phi}{KT}}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where

$$A_1 = ne \left(\frac{k}{2\pi m}\right)^{\frac{1}{2}}.$$

Here A_1 and ϕ are arbitrary constants independent of temperature, provided n be independent of temperature.

Richardson [§] then showed on the basis of purely thermo-

dynamical considerations that the emission law should be of
the form

$$I = AT^2 \epsilon^{-\frac{\phi_0}{KT}}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where A and ϕ_0 are independent of temperature.

Next he tried * to establish the relation (3) on a more
solid theoretical basis by applying the quantum theory to
the electron gas on the lines suggested and worked out by
Keesom †.   The theoretical value he obtained for A is

$$\frac{2 \cdot (2\pi)^{\frac{1}{2}}}{9} \cdot \left(\frac{3e}{5}\right)^{\frac{3}{2}} \cdot \frac{MK^2}{Nh^2} \epsilon \times \cdot 473,$$

which on numerical computation gives the value $1\cdot5 \times 10^{10}$,
a value uniformly smaller than that calculated from experi-
mental data by a factor near about $\frac{1}{10}$.

F. V. Hauer ‡ arrived at a slightly modified law from a
more phenomenological point of view.   With Herzfeld § he
set Planck's expression $\dfrac{1}{2} \cdot \dfrac{h\nu}{\epsilon^{\frac{h\nu}{KT}} - 1}$ for the kinetic energy E

of the electrons (the fraction $\frac{1}{2}$ had been introduced on the
supposition that the energy of the electrons is wholly
kinetic), and then deduced on considerations of the dis-
sociation equilibrium of ions, electrons, and atoms that the
electron concentration inside the metal should not be con-
stant but proportional to $E^{\frac{1}{2}}$, i.e. $n = n_0 E^{\frac{1}{2}}$, which at high
temperature may be taken equal to $n_1 T^{\frac{1}{2}}$, where n_1 is a constant.
This view has also been taken by J. J. Thomson in his
theory of metallic conduction.   On putting $n = n_1 T^{\frac{1}{2}}$ in
equation (1), the emission law takes the form

$$I = A_2 T \epsilon^{-\frac{\phi}{KT}}. \quad . \quad . \quad . \quad . \quad (4)$$

W. Wilson ‖, on the other hand, has calculated the
emission law on the assumption that all the radiant energy
absorbed by hot bodies is converted by quanta into the
kinetic energy of the electrons released from the metals.
He got a relation practically of the form

$$I = A_3 T^\lambda \epsilon^{-\frac{\phi}{KT}}. \quad . \quad . \quad . \quad . \quad (5)$$

* Phil. Mag. xxviii. p. 633 (1914).
† Comm. Phys. Lab. Leiden, Supp. No. 30 to Nos. 133–144 (1913).
‡ *Ann. d. Phys.* li. p. 189 (1916).
§ *Ann. d. Phys.* xli. p. 27 (1913).
‖ *Ann. d. Phys.* xlii. p. 1154 (1913) ; Royal Soc. Proc. A, xciii. p. 359
(1917).

All these formulæ with $\lambda = \frac{1}{2}$, 1, or 2 have been found to represent well the observations on thermionic currents within the range of temperatures 1000° A to 2000° A, provided the constants A and ϕ be regarded as arbitrary.

Very recently Saul Dushman * has worked out an expression for electron emission from metals as a function of temperature in the form

$$I = AT^2 \epsilon^{-\frac{L_0}{KT}}.$$

Here A is an absolute constant for all metals, and L_0 is the latent heat of evaporation of electrons at the absolute zero. The basis of his deduction is that the thermal emission of electrons from hot bodies is identical with the process of evaporation from solids or liquids. On this basis, using Nernst's heat theorem and assuming that the electrons outside the hot body behave like an ideal monatomic gas while those inside have no share in the specific heat of the body, he shows that

$$A = \frac{2\pi m e k^2}{h^3}.$$

The first assumptions have been used with success by J. Eggert † and Dr. Megh Nad Saha ‡ to calculate the degree of ionization at extremely high temperatures existing in fixed stars and the solar chromosphere. The known values of specific heats of solids also point to the correctness of the last assumption—namely, that the electrons inside a solid have no share in the specific heat of the body. But if the electrons are entirely precluded from their share in the heat motions in the solid state, it becomes difficult to explain the correctness of Wiedemann and Franz's law on the electron theory of conduction.

A better understanding can, however, be reached by the substitution of Planck's quantum expression for the energy content of the electrons inside a solid. With this substitution supplemented by the further hypothesis that the electrons emitted under thermal impulse are identical with the photoelectrons, one can easily arrive at an expression for the thermal emission in the form given by Dushman.

Theory.—We may start by supposing with Born and Kárman that the electrons inside a metal form space-lattices

* Phys. Rev. June 1923.
† *Phys. Zeits.* Dec. 1919.
‡ Phil. Mag. xl. Oct. 1920.

just as atoms do in a crystal. Then conduction is explained simply by supposing that these electron space-lattices move practically as a rigid structure relatively to the atomic lattice. In the heat motion the electron lattices naturally take part ; but the electronic vibrations on account of the smallness of electronic mass possess very high frequency, and hence these vibrations of the electrons, according to Planck's expression for energy, make no appreciable contribution to the atomic heat.

Let us now suppose that the thermal emission of electrons from metals is thermodynamically equivalent to a process of sublimation from the solid to the gaseous state. Now, classical thermodynamics give for the pressure of the vapour as a function of temperature the following equation :

$$\log_\epsilon p = -\frac{L_0}{RT} + \int_0^T \left[\frac{\int_0^T (C_p - C_f) dT}{T^2} \right] dT + C, \quad . \quad \text{(i.)}$$

where L_0 = latent heat of vaporization per gram-atom at the absolute zero ;

C_p = sp. heat per gram-atom at constant pressure of the vapour ;

C_f = sp. heat per gram-atom of the solid ;

C = chemical constant of the substance, which is thermodynamically indeterminate.

If the external electrons possess Maxwell's distribution of velocities, then $C_p = \frac{5}{2} R$. Hence equation (i.) can be written as

$$\log_\epsilon p = -\frac{L_0}{RT} + \frac{5}{2} \log T - \frac{1}{R} \int_0^T \frac{E_f dT}{T^2} + C, \quad . \quad \text{(ii.)}$$

where E_f is the energy of the condensed solid per gram-atom at $T \, °A$.

Now, supposing the electrons inside the metal to form ideal Born-Kármán crystals, we can use the following quantum theoretical value for their energy content :

$$E_f = \sum_{i=1}^{i=3N} \frac{h\nu_i}{\epsilon^{\frac{h\nu_i}{KT}} - 1}, \quad . \quad . \quad . \quad . \quad \text{(iii.)}$$

where the 3N quantities, $\nu_1, \nu_2, \nu^3{}_N$ form the elastic spectrum of the electronic vibrations.

Now

$$J = \int_0^{\mathrm{T}} \frac{h\nu}{\epsilon^{\frac{h\nu}{\mathrm{KT}}} - 1} \cdot \frac{d\mathrm{T}}{\mathrm{T}^2} = -\int_{\infty}^{x} \frac{dx}{\epsilon^x - 1} \left[x = \frac{h\nu}{\mathrm{KT}} \right]$$

$$= \left| \; \log \cdot \frac{\epsilon^x}{\epsilon^x - 1} \; \right|_{\infty}^{x} .$$

But

$$\mathrm{Lt}_{x \to \infty} \log \frac{\epsilon^x}{\epsilon^x - 1} = 0 \; ;$$

$$\therefore \quad J = \log \frac{\epsilon^{\frac{h\nu}{\mathrm{KT}}}}{\epsilon^{\frac{h\nu}{\mathrm{KT}}} - 1} . \quad . \quad . \quad . \quad . \quad \text{(iv.)}$$

Here the frequencies of the electrons stand in no known relation to atomic frequencies. But if we identify the thermally-emitted electrons with the photo-electrons, it is clear that the frequency cannot be less than the threshold frequency of the photoelectric effect, which is for various metals of the order 10^{14} to 10^{15}; hence it is easily verified that within a range of temperatures 0 to 10^4 °A, $h\nu$ is large compared with KT.

So neglecting 1 compared with $\epsilon^{\frac{h\nu}{\mathrm{KT}}}$ in (iv.), we have

$$J = \log \frac{\epsilon^{\frac{h\nu}{\mathrm{KT}}}}{\epsilon^{\frac{h\nu}{\mathrm{KT}}}} = 0$$

within the specified range of temperatures. Again, since we are here concerned only with the frequencies of those electrons which are emitted, and since for these $\nu_1, \nu_2 \ldots \nu_{3N}$ must all be greater or equal to the threshold frequency, we must have

$$\sum_{i=1}^{i=3N} J_i = 0.$$

The equation (ii.) therefore takes the form

$$\log_\epsilon p = -\frac{\mathrm{L}_0}{\mathrm{RT}} + \frac{5}{2} \log \mathrm{T} + \mathrm{C}. \quad . \quad . \quad . \quad \text{(v.)}$$

Now, according to Einstein, the kinetic energy of a

photo-electron ejected from a substance by light of frequency ν is equal to $h\nu$ less the loss of energy in getting out of the substance. The relation may be written as

$$h\nu = \phi + \tfrac{1}{2}mv^2, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \text{(vi.)}$$

where $\nu \lesseqgtr$ threshold frequency,

$\tfrac{1}{2}mv^2 =$ kinetic energy of the ejected electron,

$\phi =$ work done in tearing the electron away from the atom and in projecting it from the point at which it is torn from the atom up to the point at which it leaves the surface of the body. ϕ, in fact, corresponds to L when expressed in the same units. Since the external electrons are supposed to possess Maxwell's distribution of velocities, it is evident that at the absolute zero the electrons would escape with zero kinetic energy, and hence Einstein's relation (vi.) gives at the absolute zero

$$h\nu_0 = \phi_0 = \frac{L_0}{N},$$

where ν_0 is the threshold frequency.

The equation (v.) therefore reduces to the form

$$\log_e p = -\frac{h\nu_0}{KT} + \frac{5}{2}\log T + C.$$

Now, using the Sackur-Tetrode expression for the chemical constant of a monatomic gas, *i. e.*,

$$C = \frac{(2\pi m)^{3/2} \cdot K^{5/2}}{h^3},$$

we obtain

$$p = \frac{2\pi m^{3/2} K^{5/2} T^{5/2}}{h^3} \epsilon^{-\frac{h\nu_0}{KT}}. \quad \cdot \quad \cdot \quad \cdot \quad \text{(vii.)}$$

The number of electrons in temperature equilibrium is $n = \dfrac{p}{KT}$. But, as Richardson has shown, in thermionic currents we do not measure the number of electrons in equilibrium with the hot body, but the number emitted per unit area per sec. which, by the use of the kinetic theory of gases, is given by

$$N = n \cdot \left(\frac{KT}{2\pi m}\right)^{\frac{1}{2}} = \frac{p}{(2\pi m KT)^{\frac{1}{2}}}.$$

Hence we finally arrive at the expression for the thermionic current per sec. per unit area in the form

$$I = Ne = \frac{2\pi m e k^2}{h^3} . T^2 . \epsilon^{-\frac{h\nu_0}{KT}} \quad . \quad . \quad . \quad \text{(viii.)}$$

Comparison with Experiment.—The expression (viii.) can be written in the form

$$I = AT^2 \epsilon^{-\frac{b_0}{T}}.$$

Using the values,

$$K = 1 \cdot 372 \times 10^{-16} \text{ erg/degree,}$$
$$h = 6 \cdot 55 \ \times 10^{-27} \text{ erg/sec.,}$$
$$e = 1 \cdot 59 \ \times 10^{-19} \text{e. s. u.,}$$
$$m = 8 \cdot 995 \times 10^{-28} \text{ gram.}$$

The universal constant

$$A = 1 \cdot 80 \times 10^{11} \text{ e. s. u./cm.}^2 \text{ deg.}^2$$
$$= 60 \cdot 2 / \text{cm.}^2 \text{ deg.}^2$$

The constant $b_0 = \dfrac{h\nu_0}{K}$ may be regarded as a sort of characteristic temperature of the electrons inside the solid.

The value of b_0 has been computed from the thermionic current data of the various observers, using the expression for emission per unit area per sec. in the form

$$I = 60 \cdot 2 \ T^2 e^{-\frac{b_0}{T}}.$$

The intrinsic potentials ϕ_0 of various metals calculated both from thermionic and photoelectric data are given in the following table for comparison :—

$$\phi_0 = \frac{K b_0}{e} = \cdot 862 \times 10^{-4} \, b_0 \text{ volt } [\text{Thermionic}].$$

$$\phi = \frac{h\nu_0}{e} = \frac{hc}{e\lambda_0} = \frac{12 \cdot 36 \times 10^{-5}}{\lambda_0} \text{ volt } [\text{Photoelectric}].$$

λ_0 is the wave-length corresponding to Photoelectric threshold.

Metals.	$b_0 \times 10^{-4}$.	$\phi_0 = \dfrac{Kb_0}{e}$ volts.	*$\lambda_0 \times 10^5$ cms.	*$\phi_0 = \dfrac{Ch}{e\lambda_0}$ volts.	Resonance potential of metallic vapours.
[1] Pt............	4·925	4·25	2·80	4·42	...
[2] W............	5·260	4·53	2·20	5·70	...
[3] C	5·267	4·54	2·60	4·75	...
[4] Na	2·498	2·15	5·46	2·26	2·12
[5] Cs............	1·600	1·38	8·25	1·49	1·48
[6] Ca	3·320 ⎫	2·86 ⎫	3·70	3·34	2·85
[7] CaO	4·043 ⎭	3·48 ⎭	...	...	...
[8] MgO	3·795	3·26	3·50	3·53	2·65 ⎫ 4·42 ⎭

* Hughes's Report on Photoelectricity (Bulletin of the National Research Council, No. 10, April 1920).

[1] Schlichter, *Ann. der Phys.* xlvii. p. 129 (1908).
[2] Langmuir, *Phys. Zeits.* Jahrg. 15, p. 525 (1914).
[3] Deininger, *Ann. der Phys.* xxv. p. 285 (1908).
[4] Richardson, Phil. Trans. A, cci. p. 497 (1903).
[5] Langmuir, Science Abstracts, A, 1436 (August 1923).
[6] Horton, Phil. Trans. A, ccvii. p. 149 (1907).
[7] Deininger, *Ann. der Phys.* xxv. p. 285 (1908).
[8] Yentzsch, *Ann. der Phys.* xxvii. p. 129 (1908).

Discussion.—A glance at the table shows favourable agreement of the theory with the results of various observers on thermionic current. Unfortunately, as Hughes has pointed out in his Report on Photoelectricity, " the variations in the values for the thermionic results are only equalled by the uncertainty in the Photoelectric threshold."   Yet the order of correspondence between the values of ϕ_0 calculated from thermionic data and also from photoelectric threshold certainly justifies the assumptions involved in the deduction of the thermionic emission law.

The actual mechanism by which electrons obtain their energy for emission is, up till now, not clear. The explanation of photoelectric effect on Einstein's theory, while leading to results in good agreement with experiment, is silent about the actual processes involved.

Photoelectrons have been up till now regarded as loosely bound with the atoms, while thermally-emitted electrons

have been identified with the so-called "free electrons."
To my mind, it seems that the photoelectrons and the
electrons emitted by heat must be identical in nature in
whatever way they may exist in the metals relative to the
atomic nuclei. It seems quite possible, as Wilson con-
tends, that the actual mechanism of the thermal emission is
really a kind of auto-photoelectric resonance of the electrons
caused by the light-radiation supplied by the hot body itself.
A comparison of the resonance potentials of the alkalies and
the alkaline earth vapours with the intrinsic potential ϕ_0 is
very suggestive in this direction, and leads one to believe
that the liberating rôle is played by a resonance process.
Further speculation on this point must be deferred for the
present, for the data available are not sufficient to formulate
a definite theory on the subject.

In conclusion, I wish to record my best thanks to Prof. C.
V. Raman and Dr. P. N. Ghosh for their helpful guidance
in writing this paper.

Oct. 10, 1923.

XLIX. *The Electronic Theory of Valency.*
By B. Flürscheim, *Ph.D.*[*]

A RECENT issue of this Magazine [†] contains a paper by
Prof. Lowry, written for a discussion on Valency held
by the Faraday Society last July, and largely devoted to a
criticism of conceptions advanced by the present writer. It
may therefore be desirable to present the reply which has
been contributed to the said discussion.

Nearly all the authors of electronic valency theories have
concentrated on the "alternating effect" caused by sub-
stituents in aromatic rings. Reviewing briefly the theoretical
aspect of aromatic substitution, we shall see whether "the
introduction of an additional mechanism," in this case
electronic bonds, has brought closer agreement between
theory and facts.

The hypothesis that a substituent may cause the dis-
tribution of chemical force to alternate over a whole chain
of atoms was first advanced in 1902 [‡] and developed between

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1905 and 1910 *. The essential idea, partly based on Claus'
and Werner's general conception of the variability of the
affinity content in bonds, was this : if an atom, such as
tervalent nitrogen, with more available residual affinity than
hydrogen, is linked, for instance, to a carbon atom in benzene,
it makes a greater demand than would hydrogen on the
affinity force of this carbon atom. The equilibrium of forces
which existed in benzene is thereby disturbed, because
carbon 1 has now less affinity left to bind carbons 2. These
now have more unbound affinity available than they had in
unsubstituted benzene, and since there must be an equilibrium
between free and bound forces, the free affinity at carbons 2
and the bound affinity between carbons 2 and 3 become
greater than in benzene, and so on. It is therefore to
carbons 2 and 4 that a reacting molecule is attracted, forming
first an intermediate (Kekulé) molecular addition product,
which then changes to a substitution derivative with the new
substituent in 2 or 4. If an atom, such as pentavalent
nitrogen, disposes of less available residual affinity than
hydrogen, the reverse process occurs, with substitution in 3.

It has also been shown that the above simple principle
leaves no loophole for an arbitrary interpretation of the
relative directing effect of different substituents, and a
careful record of the numerous facts published so far has not
revealed a single proved case in disagreement with this
generalization. The writer had refrained from basing it on
any assumptions concerning the ultimate nature of chemical
affinity itself. Of late, however, others, while adhering to
this alternating principle, have stated a special case by
introducing the supposed electrical nature of chemical
affinity. " Affinity demand" has become an " electron
demand." The result would be a narrower interpretation,
but—though by no means the only possible—deeper founda-
tion, provided that agreement with chemical experimental
data remained unaffected and that the physical assumptions
were sound. Let us see whether this is the case, and first
tabulate the essential postulates of the various substitution
theories, in chronological order.

Non-electronic :—

    Flürscheim : varying alternation through varying affinity
        demand of substituting atom (named " key atom " by
        Lapworth) ; molecular addition at maximum free
        affinities.

* *Ibidem*, lxxi. p. 497 (1905); lxxvi. pp. 165, 185 (1907); Journ.
Chem. Soc. xcv. p. 718 (1909) ; xcvii. p. 84 (1910) ; *Ber. d. deutsch.
chem. Ges.* xxxix. p. 2015 (1906).

Electronic :—

Fry, Vorländer : $\pm$ alternating principle.

Lapworth, Robinson : *o-p-* : conjugated addition ; *m-* : $\pm$ alternation.

Pauly : identical with Flürscheim, excepting that key atom with affinity demand >H is defined as strongly negative atom attracting an electron.

Eastman : negativity of substituent and its size probably determine orientation.

Huggins : *o-p-* : no conjugation with ring ; *m-* : electronic conjugation with ring.

Crocker : substituting atom with electron affinity causes removal of electrons from *o-*, *p-*, and thereby *o-p-* substitution, and *vice versa.*

Lowry : $\pm$ alternation ; avoidance of crossed polarities, because less stable ; similarly polarized groups occupy metapositions ; addition at side chain or in 1 : 2 and 1 : 4 in ring may precede substitution.

A list of well over 100 facts, to be published soon, proves conclusively :

1. That there is no definite $\pm$ alternation in chains, since regarding substitution of hydrogen and replacement of substituents in aromatic rings, stability of crossed polarities, and the effect of substituents on the affinity constants of organic acids, facts are often diametrically opposed to the requirements of $\pm$ alternation ;

2. That substitution of hydrogen in the benzene ring is not preceded by 1 : 2- or conjugated addition, but by molecular addition at a single atom ;

3. That there is no regular connexion between the electropolar nature of an atom and its directing effect ;

4. That the "negativity" and size of a whole group do not determine whether it will direct to *o-p-*, or to *m-*.

In other words, not one of the above assumptions in any of the above electronic theories can bear a thorough comparison with experimental evidence. This refers, of course, to these theories as they appear to present themselves at present. In their paper before the Faraday Society, Professors Lapworth and Robinson promised further developments as to the interpretation of their theory, which will be awaited with general interest.

The physical assumptions underlying the electronic bond theories, though not so easily refutable experimentally, nevertheless appear to offer considerable logical difficulties.

To mention a few :

1. It has not been possible, so far, to devise even a hydrogen molecule model, with electron bonds, without conflicting with physical postulates.

2. Professor Lewis * has shown, using chloro-acetic acid as an example, that the electron demand of chlorine must cause a shifting of electrons toward the chlorine, therefore in *one* direction, throughout the chain. " General polarity " in Michael's sense would thereby be satisfactorily explained, including the gradual lessening of the effect with an increase in the number of intervening atoms †. Positive-negative alternation, however, pre-supposes a shifting of electrons in *opposed* directions. Since the general polar effect is admittedly always present, electrons must be shifted, simultaneously and in the same molecule, in the same and in opposed directions !

3. The idea that an atom in which an electron has been moved outward tends to slacken its hold on some of its remaining electrons is, of course, contrary to the requirements of electrostatics. It is explained by an " octet stability " assumed *ad hoc*. Since organic molecules contain atoms with substantially differing volumes and total numbers of electrons, it requires courage to assume that they all share the preference shown by many authors for the number 8 ; and that, to gratify this preference, they will set aside the fundamental law of electrostatics.

Without electronic bonds, the author has shown that it is possible to co-ordinate, not only the numerous observations on aromatic substitution, but many others, such as the thermic dissociation of quaternary compounds, equilibria in pseudo-acids and pseudo-bases, the affinity constants of organic acids and bases. His efforts in this latter direction form the subject of an interesting analysis by Professor Lowry. To reply intelligibly, the principles on which the author's co-ordination of affinity constants was based must be briefly explained.

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* Journ. Amer. Chem. Soc. xxxviii. p. 762 (1916).

† This interpretation, embodied in an advance reprint of this contribution, has since been utilized by Lapworth and Robinson, in a letter to ' Nature' (Nov. 17th, 1923). The present author disagrees, however, with certain conclusions in this letter, which appear to be based on an erroneous interpretation of Sir J. J. Thomson's deductions in the September issue of this Magazine.

Chemical reactions are, in the general case, governed by three internal factors:—

1. The *amount* of affinity available at the reacting atom (quantitative factor), which depends on the distribution of affinity force in the molecule.

2. The *kind* of affinity available at the reacting atom (polar factor = general polarity).

3. The magnitude of steric hindrance affecting the reacting atom (steric factor).

It has been shown that the relative order in which different substituents in varying positions affect each factor can be ascertained by independent evidence. There are obviously cases where one or two of these factors are practically eliminated. In the replacement of hydrogen in a mono-substituted benzene-derivative, for instance, the steric factor at the meta- and para-atoms is the same, and the polar factor differs only slightly, so that in this simplest case it was possible to predict the place of substitution (*o-p-* as against *m-*) by the quantitative factor alone, the other factors merely affecting the relative proportions of the *o-* compared with the *p-*compound.

Taking, now, an organic acid, such as propionic, and a substituent with a greater affinity demand than hydrogen, such as $-NH \cdot C_6H_5$, we have:

$$C_6H_5NH-\overset{\overset{\textstyle CH_3}{\diagup}}{CH}-\overset{\overset{\textstyle O}{\diagup}}{C}-O-H$$

and

$$C_6H_5NH-CH_2-CH_2-C\diagup\diagdown\overset{O}{\underset{O-H}{}}$$
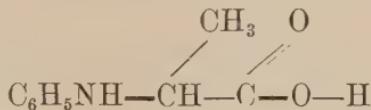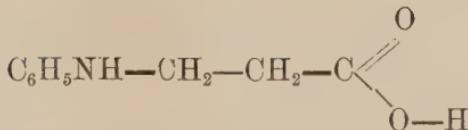
wherein thick lines denote an increased amount of bound affinity, compared with the corresponding bond in unsubstituted propionic acid, whereas thin lines denote the reverse. In the β-acid the ionizable hydrogen is therefore more strongly held than in propionic acid, and will dissociate less easily. The reverse holds for the α-acid.

The polar factor of the substituent affects the affinity of the carboxyl-oxygen for the electric charge, a "negative" substituent increasing it, and *vice versa*. Professor Lowry

maintains that the anilino-group is " negative," others may hold a contrary opinion; this question is immaterial to the present argument, since the general polar effect must be in the same direction, whatever the position of the substituent, and therefore cannot account for the fact that the α-anilino-acid is stronger, and the β-acid weaker, than propionic.

The steric factor always increases the strength of an acid, since in the electrolytic equilibrium

$$R . COOH \rightleftharpoons R . COO' + H^+$$

the unimolecular reaction from left to right is not affected by steric hindrance, whereas the bimolecular reaction from right to left is retarded thereby (solvation rendering the hydrogen ion large enough to be thus affected). Neither can the steric factor therefore account for the above inversion in β- compared with α-. This inversion would, as has just been shown, result from the quantitative factor by itself; and since tervalent nitrogen, as evidenced by its directing power in the benzene nucleus, has the greatest affinity demand, and the quantitative effect is therefore at its maximum, the resultant of all three factors also causes inversion.

Professor Lowry suggests that the low constant of the β-acid might be explained by assigning to it the constitution of an inner salt. But this is excluded. An anilino-group is incapable of forming an inner salt with a carboxyl-group. In *o*-aminobenzoic acid the dissociation constant of the amino-group is only 15 per cent. less than in the corresponding methyl-ester : in *m*-aminobenzoic acid, though its configuration is unfavourable to inner salt formation, this difference is actually greater and in the same direction. In the anilino-aliphatic acids, on the other hand, the excess of strength of the α-acid over that of the β-acid is of an entirely different order, reaching for iso-butyric acid well over 1000 per cent. Moreover, inner salts invariably melt at very high temperatures, generally with decomposition, and are more soluble in water than in organic solvents. For instance, both α- and β-aminopropionic acids—which *both* form inner salts on account of their unsubstituted (by phenyl) and therefore very much more basic amino-group— do not melt at all and are very easily soluble in cold water. But β-anilinopropionic acid melts at 59° to 60° (even lower than its α-isomeride (m.p. 162°) to which Professor Lowry does not assign an inner salt constitution), and is little

soluble in cold water, but easily in organic solvents. All these facts serve equally to disprove assumptions, similar to those of Professor Lowry, made by Vorländer [*] and by Adams [†] (to which Professor Lowry has kindly called the writer's attention).

While thus affording a striking confirmation of the above non-electronic theory, the anilino-acids—amongst others— furnish a disastrous test for electronic theories. There we have, for instance :—

$$C_6H_5 - \overset{-}{N}H - \overset{+}{C}H \underset{CH_3}{\overset{}{\diagup}} \overset{}{-} \overset{}{C} \diagdown \overset{\overset{+}{O}}{\underset{\overset{+}{O} - \overset{-}{H}}{}}$$

and

$$C_6H_5 - \overset{-}{N}H - \overset{+}{C}H_2 - \overset{-}{C}H_2 - \overset{+}{C} \diagdown \overset{\overset{-}{O}}{\underset{\overset{-}{O} - \overset{+}{H}}{}}$$
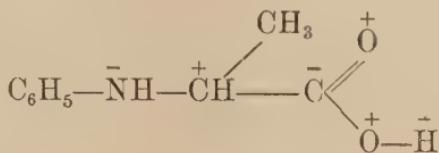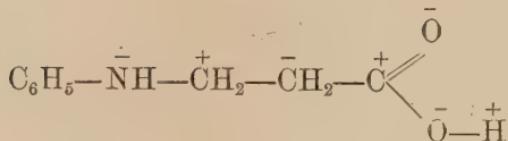
In other words, the acid which experience proves to be weaker than propionic acid should, in electronic parlance, possess carboxyl - oxygen with a particular avidity for electrons, and *vice versa*. And this, too, where we deal, for once, not with assumed, unproved electrons, but with a real, demonstrable electric charge.

In the other series of constants discussed by Professor Lowry, most of the values differ relatively little, and in no case is there a substituent with such an outstanding quantitative effect as that of tervalent nitrogen. In such cases the application of all three factors cannot leave the quantitative effect in such a predominant position, as a glance at the author's papers of 1909 and 1910 will show, where all three factors have been applied to numerous constants (including the anilino-acids), by a concordant method throughout which automatically excludes arbitrary adjustments. Professor Lowry proves that the application of the quantitative factor alone does not yield general agreement—a fact not only in conformity with the author's theory, but postulated by it.

[*] *Lieb. Annalen*, cccxx. p. 99 (1902).
[†] Journ. Amer. Chem. Soc. xxxviii. p. 1508 (1916)

It can be shown that when all three factors are applied, all the constants examined by Professor Lowry are in agreement with the theory, subject to the following remarks :

1. For vinylacetic acid, Fichter's value ($3·8 \times 10^{-5}$) should be replaced by Zelinsky's re-determination ($4·65 \times 10^{-5}$).

2. As to unsaturated acids, in general, one must agree with Professor Lowry that there is uncertainty where only one of the two cis-trans-isomerides is known. But it can be shown that this affects only $\alpha\beta$-unsaturated acids.

3. That according to the author's theory n-valeric acid must not be stronger than n-butyric acid, is also a point on which Professor Lowry is quite correct. All the published comparative determinations for these two acids have therefore been examined. There are three from Ostwald's laboratory :

	N-Butyric.	N-Valeric.	Date.
1	$1·49 \times 10^{-5}$	$1·61 \times 10^{-5}$	1889
2	$1·52 \times 10^{-5}$	$1·50 \times 10^{-5}$	1895
3	$1·75 \times 10^{-5}$	$1·56 \times 10^{-5}$	1905

In addition, there are constants by Billitzer :

| 4 ...... | $1·54 \times 10^{-5}$ | $1·61 \times 10^{-5}$ | 1899 |

The discrepancies are therefore considerable, but only in No. 2 (Francke) have *both* acids been carefully purified. There is, at any rate, no reason to conclude that n-valeric is stronger than n-butyric acid. But butyric, in spite of the positive effect of methyl, should be and is somewhat stronger than propionic acid (steric effect of β-substituent, see 1909 paper, p. 729).

To summarize : organic facts can be concordantly co-ordinated on the basis of varying affinity demand in conjunction with general polarity and steric hindrance. Electronic bonds, however, are confronted with serious difficulties by the facts of organic chemistry as well as by the postulates of physics.

Fleet, Hampshire.

L. *A New Form of Electrometer.*
By F. A. & A. F. LINDEMANN *and* T. C. KEELEY *.

[Plate II.]

A S was shown in a paper published some years ago †
numerous problems in astrophysics could be solved if
a convenient photoelectric method were developed for
measuring the amount of light received from stars, nebulæ,
comets, etc. For this purpose the photoelectric cell is best
fixed just behind the focus of an equatorial telescope and the
current produced by the light which falls upon the cell is
measured by means of an electrometer. In order to keep
the electrostatic capacity of the system as small and constant
as possible, it is desirable to fix the electrometer and the cell
rigidly together. This also facilitates drying and thus
diminishes any leakage. This arrangement involves con-
siderable difficulties, however, since no existing form of
electrometer maintains a constant sensitivity, and still less a
steady zero, when moved about at the end of an equatorial
telescope. The object of this paper is to describe a new form
of electrometer which is free from these defects. Since it is
capable of a sensitivity as great as that of any existing
electrometer, although its period is less than one second and
its capacity less than 2 cm., it may be useful for many
laboratory purposes even where independence of the zero
and sensitivity to tilt is not essential.

The principle of this electrometer is the same as that of
the quadrant electrometer ; it consists essentially of a needle,
which in this case really has the shape of a needle, suspended
at its centre on a torsion fibre in such a way that it can
rotate between four cross-connected plates which take the
place of the ordinary quadrants. The important innovation
is that the torsion fibre is fixed at both ends under tension so
that the centre of rotation of the needle is fixed, and its
rotation can therefore be determined by observing the motion
of one end through a microscope. This renders a mirror
unnecessary, and, consequently, the moment of inertia of the
moving parts can be reduced to a minimum. Hence a very
small torsional restoring force may be used without in-
creasing the period unduly.

The most suitable dimensions can be found by considering

the sensitivity in terms of the dimensions of the various parts. If r_1 is the radius of the torsion fibre, l_1 its semi-length, and n_1 the torsion modulus, the restoring couple for unit angular displacement is $\Gamma_0 = \dfrac{\pi n_1 r_1^4}{l_1}$. If r_2 is the effective radius of the needle, l_2 its semi-length, and ρ_2 its density, the moment of inertia I is $\frac{2}{3}\pi\rho_2 r_2^2 l_2^3$. Hence the free period *in vacuo* will be

$$T_0 = 2\pi\sqrt{\frac{I}{\Gamma_0}} = 2\pi\sqrt{\frac{2\rho_2 r_2^2 l_2^3 l_1}{3 n_1 r_1^4}} \quad . \quad . \quad . \quad (1)$$

If an earthed conductor of capacity C in an electric field F be moved a distance δ in the direction of the field a charge $C.\delta.F$ will be induced upon it, assuming its reaction on the field to be negligible. Hence if c_2 be the capacity of the needle per unit length, rotation through an angle θ will induce a charge $\theta l_2 c_2 F dl$ in each element dl. The electric field therefore tends to make the needle unstable, the couple to which it gives rise being $2F\displaystyle\int_0^{l_2} \theta l_2 c_2 F dl$, which reduces for unit angular displacement to $\frac{2}{3}c_2 F^2 l_2^3$. Hence the effective restoring couple Γ will be Γ_0 diminished by this electric couple, *i.e.* $\Gamma = \dfrac{\pi n_1 r_1^4}{l_1} - \frac{2}{3}c_2 l_2^3 F^2$. The period in the field therefore, if damping be neglected, will be

$$T_1 = 2\pi\sqrt{\frac{2\rho_2 r_2^2 l_2^3}{3\left(\dfrac{\pi n_1 r_1^4}{l_1} - \frac{2}{3}c_2 l_2^3 F^2\right)}} = 2\pi\sqrt{\frac{2\rho_2 r_2^2 l_2^3 l_1}{3\pi n_1 r_1^4 - 2c_2 l_2^3 F^2 l_1}}$$

$$. \quad . \quad . \quad . \quad (2)$$

If a charge at potential v is communicated to the needle, each element dl will contain a quantity of electricity $vc_2 dl$. The turning moment in a field F will therefore be

$$2\int_0^{l_2} vF c_2 l \, dl = vF c_2 l_2^2,$$

taking account of both arms of the needle. Hence the needle will turn through an angle $\theta = \dfrac{vF c_2 l_2^2}{\Gamma}$ and its end will be displaced by a charge at unit potential through a distance

$$\frac{\theta l_2}{v} = \frac{3F c_2 l_2^3 l_1}{3\pi n_1 r_1^4 - 2c_2 l_2^3 F^2 l_1} = \frac{3F c_2}{8\pi^2 \rho_2 r_2^2} . T_1^2 . \quad . \quad (3)$$

This quantity may be regarded as a measure of the sensitivity of the instrument. The number of divisions per volt depends simply upon the magnification which can be obtained with the microscope used.

At first sight it might appear that one could increase the sensitivity for a given period almost indefinitely by increasing the field F and diminishing the effective radius of the needle r_2.

This is not true, however, because a lower limit to r_2 is imposed by various considerations. For the purpose for which the electrometer was originally designed it was necessary that its zero and sensitivity should not be materially altered when the equatorial to whose end it was fixed was directed at different celestial objects. Hence it was important that the needle should not bend appreciably under its own weight. If the maximum displacement of the end when the electrometer is rotated which one decides to admit is called δ_2 this fixes a lower limit to $r_2 = l_2^2 \sqrt{\dfrac{\rho_2 g}{2 \mathrm{E} \delta_2}}$, E being, of course, Young's modulus.

Even if one is content to use the electrometer in one position and thus is able to neglect the effect of gravity, it is not possible to reduce r_2 indefinitely. All the above calculations are made on the assumption of a rigid needle. If the needle is too thin it will bend under the electric force acting on its own induced charge. It is obviously essential that the needle should not become unstable under these conditions, and it is undesirable that this electrostatic bending should be comparable to the torsional deflexion. The amount of bending which occurs under the electric force is somewhat complicated to calculate accurately, since the charge generated is proportional to the displacement. The order of magnitude of the quantities involved may be estimated, however, by considering that half the capacity of the needle is effective, and that this, with the corresponding charge, is placed at the end of the needle. In this case the charge induced by the bending of the end through a distance δ is $\frac{1}{2}l_2 c_2 \mathrm{F} \delta$, and the force which comes into play is $\frac{1}{2}l_2 c_2 \delta \mathrm{F}^2$. As the restoring force is $\dfrac{3\pi r_2^4 \mathrm{E}\delta}{4 l_2^3}$ the needle becomes unstable if

$$\tfrac{1}{2}l_2 c_2 \mathrm{F}^2 > \frac{3\pi r_2^4 \mathrm{E}}{4 l_2^3}.$$

In practice the limit of r_2 which was used was that set by

the gravitational bending. Taking the permitted shift of the zero when the electrometer is reversed as 10^{-3} cm. this leads to a value of r_2 large enough to be stable for fields up to 10 E.S.U., *i. e.* 3000 volts per cm., and fields greater than this are not usually convenient to use.

If one inserts the above value for r_2 in the equation for the sensitivity $\dfrac{\theta l_2}{v} = \dfrac{3 F c_2}{8 \pi^2 \rho_2 r_2{}^2} \cdot T_1{}^2$, one finds

$$\frac{\theta l_2}{v} = \frac{3 T_1{}^2}{8 \pi \rho_2 l_2{}^2} \sqrt[4]{\frac{3\pi}{2}} \cdot E F^2 c_2{}^3.$$

It is evident from this that the sensitivity may be increased by reducing l_2, but here again one cannot proceed to extremes.

A limit is set by the technical difficulty of constructing an instrument on a very small scale. The quadrants, or rather plates, cannot be too close together, as the needle must be mounted between them. But the plates acting upon the other end of the needle must be at such a distance from the first pair that their field is not disturbed unduly. Hence the pairs of plates must be at a distance from one another great compared to the distance between the two plates in a pair, and this makes it impossible to use a very short needle, *i. e.* reduce l_2 indefinitely.

As a matter of fact, the optimum conditions according to this formula are not of great practical importance, since air-damping, which has been treated as negligible above, becomes extremely important when the restoring force is very much reduced. It is true that the suspension can be enclosed in an air-tight box and the air removed, but the considerable increase in sensitivity so attained rarely makes up for the inconvenience this method involves. For most purposes it is preferable to avoid a vacuum, even at the expense of sensitivity, and to choose the dimensions of fibre and needle with a view to obtaining the best conditions of sensitivity and period in air at ordinary pressure.

If the damping per unit length is μr_2 the damping couple on the needle will be $2 \displaystyle\int_0^{l_2} \mu r_2 l \cdot l\dot\theta\, dl = \tfrac{2}{3}\mu r_2 l_2{}^3 \dot\theta = \kappa \dot\theta$. The equation of motion therefore becomes $\ddot\theta + \dfrac{\kappa}{I} \cdot \dot\theta + \dfrac{\Gamma}{I} = 0$, which reduces, in the case of heavy damping, to $\theta = \theta_0 e^{-\frac{\Gamma}{\kappa} \cdot t}$.

If t_0 represents the time in which the deviation from the final position is reduced from θ_0 to $\dfrac{\theta_0}{e}$, then

$$t_0 = \frac{\kappa}{\Gamma} = \frac{2\mu r_2 l_2{}^3 l_1}{3\pi n_1 r_1{}^4 - 2c_2 l_2{}^3 F^2 l_1}.$$

Hence, from (3)

$$\frac{\theta l_2}{v} = \frac{3 F c_2 t_0}{2\mu r_2}.$$

In general F will be increased to a value near the unstable value where $3\pi n_1 r_1{}^4 = 2c_2 l_2{}^3 l_1 F^2$. If this value is inserted the above expression may be reduced to

$$\frac{\theta l_2}{v} = \sqrt{\frac{9\pi^3 c_2 \rho_2}{\mu^2}} \cdot \frac{t_0}{T_0}.$$

Since $c_2 \left(= \dfrac{1}{2 \log \dfrac{l_2}{r_2}} \right)$ scarcely varies and ρ_2 and μ cannot

be altered very much, it is evident that the maximum sensitivity goes up as the period *in vacuo* is diminished. It must be remembered, however, that the field on the plates goes up in the same proportion as shown in the previous formula. It follows that for a given field the maximum sensitivity is reached when the diameter of the needle is a minimum. The diameter of the needle is determined by the condition that it must not bend more than a certain amount, being roughly given, as shown above, by $r_2{}^4 = \tfrac{2}{3} \cdot \dfrac{c_2 F^2}{\pi E} \cdot l_2{}^4$. Hence the limiting sensitivity is given by

$$\frac{\theta l_2}{v} = \sqrt[4]{\frac{243}{32} \cdot F^2 c_2{}^3 \pi E} \cdot \frac{t_0}{\mu l_2}.$$

As was remarked above, l_2 cannot be reduced inordinately owing to constructional difficulties. Hence the sensitivity can only be increased, without sacrificing rapidity of working, by increasing the field. In principle, of course, this could be made equal to the sparking potential. In practice it is more convenient to work with much lower fields, since, as stated, the distance between the plates must be some 4 to 6 mm., and a large field would therefore entail a very large battery or other source of constant high potential.

The form finally adopted for general use is shown in figs. 1 and 2, Pl. II. In this instrument the silica torsion

fibre A (much exaggerated in the illustration to render it visible) is about 1·4 cm. long and 6μ thick, and is stretched under a tension of about half the breaking strain on a U-shaped frame B. This is made of 3 mm. silica rod with saw-slits about 1 mm. deep at the ends in which the fibre is mounted. As the frame and the fibre are both of silica no change of tension occurs when the temperature changes.

The fibres are silvered by sputtering in the usual way, and one end is fixed in the slit with Wood's metal. A thin copper wire is inserted in the slit at the same time forming the lead. The other end of the torsion fibre is fixed in the other slit with shellac. In order to assure the necessary tension, a weight of appropriate size is attached temporarily to the protruding end and the shellac melted with the frame in a vertical position. When it has re-solidified, the protruding portion is removed.

In order to facilitate balancing, the needle C is composed of two equal parts placed parallel to one another on each side of the torsion fibre. They were usually about 25μ thick and 2 cm. long and made of silvered glass. The ends are sealed together, and the whole attached in the plane of the frame rigidly to the torsion fibre by electrolytically deposited copper.

The quadrants D consist of plates about 1·5 cm. broad and 1 cm. high, in which slots are cut about 2 mm. broad through which the needle can pass. These plates are mounted about 5 mm. apart on 3 mm. silica rods, E. The suspension is mounted between them so that the centre of rotation coincides with the centre of symmetry of the four plates. The whole is enclosed in a small metal box about 4·5 cm. long by 2·8 cm. broad and 3 cm. high, made of a suitable aluminium alloy, in the centre of the top and bottom of which are holes about 10 mm. in diameter closed with microscope cover-slides. The leads from the two sets of plates are carried out at one end insulated by silica tubes, the lead from the needle being carried out, similarly insulated, at the other. An earthing terminal on the box enables the effect of stray electrostatic fields to be eliminated.

For use, this box—which only weighs about 80 grammes—is placed on an ordinary microscope stand and the pointer at the upper end of the needle is observed, illumination being obtained in the ordinary way through the hole in the bottom of the box. The connexions can, of course, be made in any of the ways used in ordinary quadrant electrometers. On account of the small restoring force and moment of

Fig. 1.
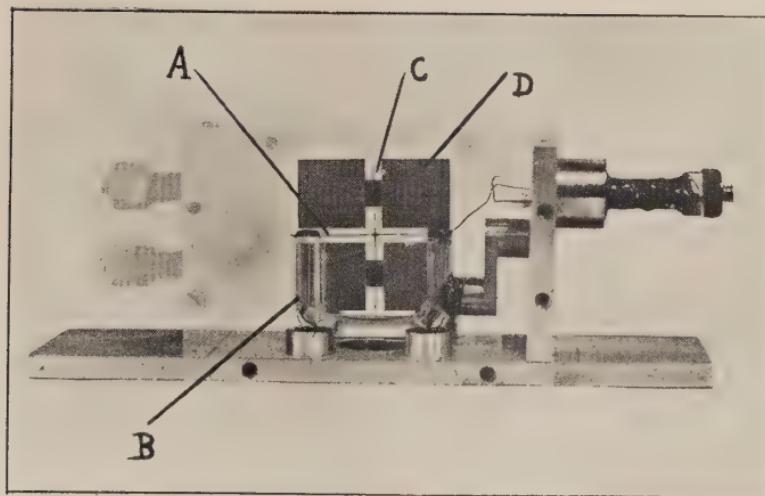
Fig. 2.
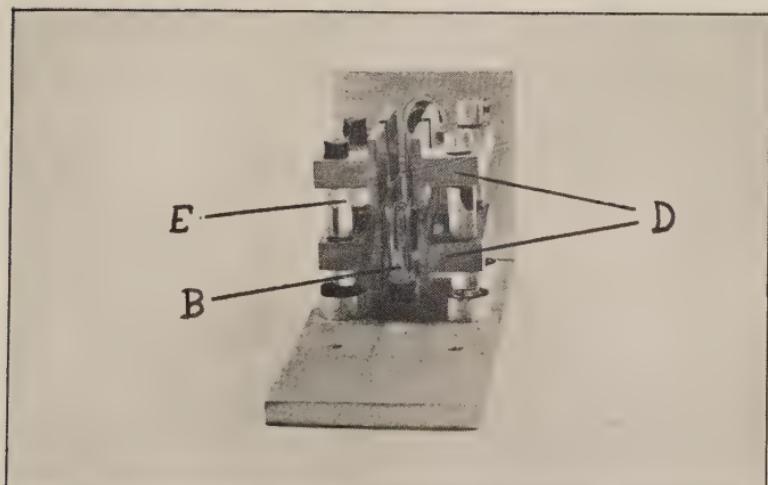
inertia, air-damping with the above dimensions is about right to render the instrument practically aperiodic.

For use on an equatorial the microscope was permanently fixed to the lid of the box and artificial light from a small four-volt lamp used. In order to facilitate setting the zero and varying the sensitivity, the plates were further made movable on slides, their positions being adjusted by screws with divided drums, passing through the sides of the box. The whole electrometer was then screwed onto the brass cell box, in which the photoelectric cell was mounted, and this was rigidly attached to the equatorial. For general use, the form described above is, however, probably preferable on account of its simplicity : adjustment of zero and sensitivity can be accomplished by altering the potentials on the plates, fine adjustment by means of a potentiometer in the middle of the high tension batteries being advisable.

The constants of the instrument are in reasonably close agreement with the formulæ developed above. For the sake of completeness the exact constants of one instrument may be given. The torsion fibre is 1·4 cm. long and about 6 μ thick. The needle consists of two silvered glass fibres 0·9 cm. long and 17 μ thick. The plates are 0·6 cm. apart, and the instrument becomes unstable at about 100 volts. The capacity is 1·3 cm. and the free period (calculated *in vacuo*) is about 0·15 second. The zero moves about ·06 mm. on turning the instrument through 90°, ·000 mm. for 180°, ·008 mm. for 270°. The sensitivity is completely independent of tilt. With a field of 160 volts/cm., corresponding to a potential of 97 volts, the deflexion reaches $\frac{99}{100}$ of its final value in about one second. The pointer moves 0·76 mm. per volt with this field, so that with a $\frac{1}{4}$-inch objective and a × 20 eyepiece a sensitivity of 450 divisions per volt can be attained. Under these conditions perfectly satisfactory definition can be obtained and $\frac{1}{10}$ of a division can be read without difficulty. As is evident, no attempt was made to use a very strong field. In most cases one or two sixty-six volt boxes, such as are on sale for wireless sets, sufficed. If desired, one can use a finer torsion fibre and batteries of ten or twelve volts across the plates. With a suitable leak these electrometers, of course, make very convenient quick period galvanometers, sensitive to currents of 10^{-10} to 10^{-14} ampere, and as the sensitivity is almost equal to that of a Dolezalek electrometer with a very much smaller capacity and period, it would seem that it may be useful for many purposes, even where convenience in using is not so much an object as great sensitivity and accuracy.

LI. *Note on Mr. Harward's Paper on the Identical Relations in Einstein's Theory.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN a paper on "The Identical Relations in Einstein's Theory" in the August 1922 number (pp. 380–382) of the Philosophical Magazine, Mr. Harward proves a general theorem which he discovered for himself, although he did not believe it to be undiscovered before. The theorem is:

$$(B_{\mu\nu\sigma}^{\rho})_{\tau} + (B_{\mu\sigma\tau}^{\rho})_{\nu} + (B_{\mu\tau\nu}^{\rho})_{\sigma} = 0.$$

It may be of interest to mention that this theorem is known, especially in Germany and Italy, as "Bianchi's Identity," having been published by L. Bianchi in the *Rendiconti Acc. Lincei*, xi. (5) pp. 3–17 (1902). In this paper, Bianchi already deduced from this theorem the identity Mr. Harward refers to:

$$G_{\mu\nu}^{\nu} = \tfrac{1}{2}\frac{\partial G}{\partial x^{\mu}}.$$

The identity of Bianchi seems, however, to be published for the first time by E. Padova (*Rendiconti Acc. Lincei*, v. (4) pp. 174–178, 1889), who obtained it from G. Ricci. Compare for this the book of Struik (*Grundzüge der mehrdimensionalen Differentialgeometrie*: Berlin, J. Springer, 1922, p. 148), where the theorem is proved in a similar way as Mr. Harward does. A similar proof was already given by Schouten (*Mathem. Zeitschr*. xi. pp. 58–88, 1921).

The theorem can be generalized by taking geometries with a more general parallel displacement than in ordinary Riemann geometry. We then obtain the generalized geometries of Schouten (*Mathem. Zeitschr*. xiii. pp. 56–81, 1922), of which the geometries of Weyl and Eddington (*cf.* Eddington's 'Mathematical Theory of Relativity,' Ch. vii.) are special cases. Schouten, in a recent paper (*Mathem. Zeitschr*. xvii. pp. 111–115, 1923), proved the generalization of Bianchi's Identity for a geometry of which a geometry with a symmetrical displacement (that is, a geometry in which $\Gamma_{\nu a}^{\mu} = \Gamma_{a\nu}^{\mu}$, *cf.* Eddington, *loc. cit.* p. 214) is a special case. This special case is treated by A. Veblen (Proc. Nat. Ac. of Sciences, July 1922). R. Bach already gave the generalization for the geometry of Weyl (*Mathem. Zeitschr*. ix. pp. 110–135, 1921).

A simple proof of Bianchi's Identity, which holds for a

geometry with a symmetrical displacement and was suggested to us by Prof. Berwald at Prague, can be given in the following way :—

Let $\Gamma^\mu_{\nu a} = \Gamma^\mu_{a\nu}$.

We can introduce in this case, in a regular point $x_0{}^\nu$, a system of so-called geodesic coordinates $'x^\nu$, by the transformation :

$$x^\nu - x_0{}^\nu = 'x^\nu - \tfrac{1}{2}\Gamma^\nu_{\lambda\mu}\, 'x^\lambda\, 'x^\mu$$

(*cf.* Weyl, *Raum, Zeit, Materie*, 4th edition, §14, p. 101).

For these coordinates, all $\Gamma^\mu_{\nu a}$ vanish in $x_0{}^\nu$, and covariant differentiation in $x_0{}^\nu$ becomes identical with ordinary differentiation.

When now we evaluate the expression

$$(R^\rho_{\mu\nu\sigma})_\tau + (R^\rho_{\mu\sigma\tau})_\nu + (R^\rho_{\mu\tau\nu})_\sigma \quad . \quad . \quad . \quad (1)$$

for the generalized Riemann-Christoffel symbols

$$R^\rho_{\mu\nu\sigma} = \left(\frac{\partial}{\partial x^\nu}\,\Gamma^\rho_{\mu\sigma} - \frac{\partial}{\partial x^\sigma}\,\Gamma^\rho_{\mu\nu}\right) + \left(\Gamma^\rho_{\kappa\nu}\,\Gamma^\kappa_{\mu\sigma} - \Gamma^\rho_{\kappa\sigma}\,\Gamma^\kappa_{\mu\nu}\right),$$

all terms with $\Gamma^\mu_{\nu a}$ and $\dfrac{\partial}{\partial x^\lambda}\,\Gamma^\mu_{\nu a}$ vanish in $x_0{}^\nu$, and only the following expression remains :

$$\frac{\partial^2}{\partial x^\tau \partial x^\nu}\Gamma^\rho_{\mu\sigma} - \frac{\partial^2}{\partial x^\tau \partial x^\sigma}\Gamma^\rho_{\mu\nu} + \frac{\partial^2}{\partial x^\nu \partial x^\sigma}\Gamma^\rho_{\mu\tau} - \frac{\partial^2}{\partial x^\nu \partial x^\tau}\Gamma^\rho_{\mu\sigma}$$
$$+ \frac{\partial^2}{\partial x^\sigma \partial x^\tau}\Gamma^\rho_{\mu\nu} - \frac{\partial^2}{\partial x^\sigma \partial x^\nu}\Gamma^\rho_{\mu\tau},$$

which vanishes identically. Hence also (1) vanishes identically.

Yours faithfully,

J. A. SCHOUTEN,
D. J. STRUIK.

Delft, April 28, 1923.

P.S. *February* 7, 1924.—A generalization of Bianchi's identity for a geometry with a non-symmetrical displacement is found in Weitzenböck, *Invariantentheorie* (P. Noordhoff, Groningen, 1923, p. 357). The above given proof of the identity occurs also in the quoted paper of Veblen. For a generalization for the geometry with the most general linear displacement see the book of Schouten, '*Der Ricci-Kalkül*,' that will soon appear in Springer's series : *Die Grundlehren der mathematischen Wissenschaften.*

L11. *On the Origin of certain Spectral Lines hitherto attributed to Oxygen. By* W. Jevons, *A.R.C.Sc., M.Sc., Lecturer in Physics, Artillery College, Woolwich* *.

CERTAIN lines in the ultra-violet have been attributed by Schniederjost † to the so-called "compound line spectrum" of oxygen, which is now known as O.1 ‡ and ascribed to the neutral atom of oxygen. Professor Fowler in his Report § makes the following reference to these lines :—
" A considerable number of lines of O.1 have been observed in the ultra-violet by Schniederjost, but their relation to the established series, if any, has not yet been traced. The wave-lengths of these lines are included in the table of unclassified lines " ‖. It is the object of this paper to offer new evidence as to the origin of these lines, concerning which Schniederjost would seem to have been misled.

In the course of an investigation of the ultra-violet line spectrum of chlorine by the present writer ¶, a number of well-defined bands were observed in the condensed discharge through a chlorine tube which was known to contain carbon, hydrogen and oxygen as impurities. The heads of these bands degraded towards the red, and their line-structure was clearly shown. A close agreement of wave-length was found between these band-heads and some of the more refrangible of Schniederjost's O.1 lines, and some doubt was felt, therefore, as to the real existence of the latter. An attempt was then made to observe them in the oxygen spectrum. For this observation a continuous flow of oxygen, prepared by the electrolysis of barium hydroxide solution and dried by phosphorus pentoxide, was passed through a length of capillary tube, then through a discharge-tube with a quartz window end-on to the capillary, and finally to a pump which was kept in action throughout each exposure in a

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small Hilger quartz prism spectrograph. Though lines of the established O.I series * were well developed, only one line was detected in a position given in Schniederjost's O.I list (Table I. column 3), namely $\lambda_{R.A.}$ 2883·93 (4). which is also given as an oxygen line by Runge and Paschen † at $\lambda_{R.A.}$ 2883·95 (6). Prof. Fowler's oxygen observations ‡ not only confirm this result, but also indicate that $\lambda_{R.A.}$ 2883·93 may be an enhanced (O.II) rather than an O.I line.

The observed bands already mentioned have now been recognized as some of Deslandres' First Negative bands of carbon §. The close agreement between Deslandres' and Schniederjost's wave-lengths in columns 1 and 3 of Table I. leaves little doubt as to the identification of sixteen of Schniederjost's lines with Deslandres' band-heads.

Three of Schniederjost's wave-lengths not thus correlated show some agreement with those of three band-heads (in column 2) belonging to another of Deslandres' carbon band-systems, namely the Fourth Positive ‖. The agreement is not so good as in the case of the First Negative bands, owing perhaps to the lesser degree of accuracy attainable at the time of the pioneer measurements (1888).

If these identifications be accepted there remain only five of Schniederjost's measures to be accounted for; namely vv 34529·1, 34691·1, 34970·7, 36915·6, 37403·0 (see Table I. column 4). The question of these may be approached, and at the same time the band-like distribution of the majority of Schniederjost's "lines" be demonstrated, by arranging the wave-numbers (column 4) in the manner first employed by Deslandres for the First Negative and other band systems, and subsequently by many other observers. The scheme is such that the first differences of the wave-numbers form arithmetical progressions in horizontal rows and vertical

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* See Tables in Prof. Fowler's Report, pp. 167 & 168. Paschen and Götze, 'Seriengesetze der Linienspektren' (Berlin, 1922), pp. 136–138; and W. M. Hicks, 'Analysis of Spectra' (C.U.P. 1922), pp. 298 & 299.

†*Ann. d. Phys.*, lxi. p. 647 (1897); Astrophys. Journ., viii. p. 70 (1898). See also Kayser's *Handbuch*, vi. p. 213.

‡ Unpublished but kindly placed at the author's disposal by Professor Fowler.

§ H. Deslandres, *Comptes Rendus*, cxxxvii. p. 460 (1903); see also Kayser's *Handbuch*, v. p. 233.

‖ H. Deslandres, *Comptes Rendus*, cvi. p. 842 (1888); *Annales de Chim. et de Phys.*, (6) xv. p. 85 (1888). See also Kayser's *Handbuch*, v. p. 233.

TABLE I.

1		2		3		4	5	6	7
Heads of First Negative Bands. (Deslandres.)		Heads of Fourth Positive Bands. (Deslandres.)		O.I Lines (Schniederjost).					Notes.
$\lambda_{R.A.}$	Int.	$\lambda_{R.A.}$	Int.	$\lambda_{R.A.}$	Int.	$\nu_{vac.}$ $=10^8/\lambda_{I.A.\,vac.}$	Group n p (See Table II.)	$\nu_{obs.}$ $-\nu_{calc.}$	
2897·11	10			2897·42	2n	34504·7			*a*
				95·37	3	34529·1			
83·86	10			83·93	4	34666·1			*a, b*
				81·85	2n	34691·1	II 67 32	+4·3	
				58·81	1	34970·7			
2786·51	1			2786·17	1	35882·3	IV 66 30	+1·0	
53·65	1			53·47	1	36308·5	III 67 31	−1·5	
23·06	3			22·57	1	36720·5	II 68 32	+2·3	*c*
				08·18	1	36915·6			
2694·80	2						I 69 33		*d*
				2672·89	1	37403·1	V 66 29	−0·7	
39·63	4			39·00	2	37883·3	IV 67 30	+0·5	
07·95	4			07·51	2	38340·7	III 68 31	−0·6	
2578·39	6			2577·93	2	38780·9	II 69 32	+1·5	
51·20	5			50·64	1	39195·5	I 70 33	−1·6	
05·39	3			04·67	2	39914·8	IV 68 30	+0·7	
2475·10	4			2474·45	2	40402·1	III 69 31	−0·5	
46·69	8			46·05	3	40871·2	II 70 32	+0·6	
20·29	8			19·64	3	41317·3	I 71 33	−0·8	
2353·23	4			2352·61	2	42494·4	III 70 31	+0·7	*e*
25·93	·7			23·34	2	42992·7	II 71 32	+1·1	
2300·36	7			2299·93	3	43467·5	I 72 33	−1·5	
		2215·3	10	14·62	2	45141·8	II 72 32	−0·7	
2190·51	4			2189·99	2	45649·4	I 73 33	−0·4	
		2136·5	2	37·6	1	46768·8			
		12·7	8	12·4	1	47326·7	II 73 32	−3·4	

Notes to Table I. (column 7.)

(*a*) Deslandres points out that these two bands differ from the remainder in two respects : (i.) the two strong heads are degraded in both directions, while the others are degraded towards the red, and (ii.) they cannot be included in the same group scheme (see Table II.) with the others.

(*b*) Also observed as an oxygen line by Runge and Paschen (*loc. cit.*), Professor Fowler, and the author.

(*c*) The measure published by Schniederjost is $\lambda_{R.A.}$ 2723·57, whence $\nu_{vac.}=36707\cdot0$ cm.$^{-1}$. There is, however, some reason (which will become clear from Table II.) for believing that this wave-length is 1 unit too high. The modified value has been entered in this table. The difference from Deslandres' corresponding wave-length is not thereby altered in magnitude but only in sign, and the sign is brought into agreement with that of the corresponding differences ($\lambda^{Desl.} - \lambda_{Schn.}$) for the other heads.

(*d*) For easy reference to Table II. it may be noted here that the wave-number derived from Deslandres' λ for this head is $\nu_{vac.}$ 37098·8.

(*e*) Given by Miss G. V. Morrow [Sci. Proc. Roy. Dublin Soc., xiii. p. 615 (1913)] as $\lambda_{R.A.}$ 2352·6 (4), with a note that, though the line has been attributed to gold, it is more probably due to oxygen. It may be noted here also, that the line $\lambda_{R.A.}$ 2478·7 (5 attributed to oxygen by Miss Morrow is really a well-known carbon line.

n (column 3)=nebulous

columns, as in Table II. in which Deslandres' numbers I–IV for the vertical groups are retained.

TABLE II.

n	I		II		III		IV		V
	p 33		32		31		30		29
73	(2) 45649.4	1677.3	(1) 47326.7 g						
	2189.9		2184.9						
72	(3) 43467.5	1674.3	(2) 45141.8 g						
	2150.2		2149.1						
71	(3) 41317.3	1675.4	(3) 42992.7						
	2121.8		2121.5						
70	(1) 39195.5	1675.7	(3) 40871.2	1623.2	(2) 42494.4				
	2089.5 d		2090.3 (2)		2092.3 (2)				
69	[37106.0] d	1674.9	38780.9 (2)	1621.2	40402.1 (2)				
			2060.4		2061.4				
68			(1) c 36720.5	1620.2	(2) 38340.7	1574.1	(2) 39914.8		
			2029.4 (2n)		2032.2 (1)		2031.5 (2)		
67			34691.1	1617.4	36308.5 (1)	1574.8	37883.3 (2)		
							2001.0 (1)		
66							35882.3 (1)	1520.7	37403.0 (1) f

Notes to Table II.

( ) Intensities by Schniederjost.

c Modified value of $\nu_{vac.}$ used instead of 36707.0 (see note c to Table I.).

d Not observed by Schniederjost. The value of $\nu_{vac.}$ from Deslandres' observation is 37098.8 (see note d to Table I.).

[ ] Computed $\nu_{vac.}$ (formula, page 590).

f Not observed by Deslandres.

g Not observed as First Negative band-heads by Deslandres, who, however, gives Fourth Positive band-heads at about these positions (see Table I. column 2).

From this table the following conclusions may be drawn :—

1. One of the five outstanding wave-numbers, namely ν 37403.0, represents a previously unobserved head, falling in a new group (V) of the extended Deslandres' First Negative system.

2. Another of them, namely ν 34691.1, probably represents an extension of Group II ; the slight discrepancies in intensity and wave-number being due perhaps to the nebulous character of the observed " line."

3. The remaining three $\nu\nu$ 34529.1, 34970.7, and 36915.6 appear to be definitely excluded from the First Negative carbon system.

4. There is a possible alternative allocation of two of the three measures, which have been already correlated (page 587) with three of Deslandres' Fourth Positive band-heads.

These two are $\nu\nu$45141·8 and 47326·7, which are shown as a possible extension of Group II.

Schniederjost's wave-numbers in Table II. are very closely represented by an empirical formula of the type commonly employed for band systems, namely :—

$$\nu = 14·944\,(n + 0·4655)^2 - 25·177\,(p + 0·7344)^2 - 6354·0$$

in which n and p take successive integral values, the former from 66 to 73, and the latter from 29 to 33, as shown in both tables. The residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) are given in Table I. (column 6).

In conclusion, then, it seems almost certain that, of Schniederjost's twenty-five O.I observations twenty-one are not to be associated with oxygen at all but are good measures of Deslandres' carbon band-heads in the same region, carbon being a very frequent impurity in discharge tubes. $\lambda_{\text{R.A.}}$ 2883·93 is a genuine oxygen line confirmed by the observations of Runge and Paschen, Prof. Fowler, and the present writer. The three at $\lambda\lambda_{\text{R.A.}}$ 2895·37, 2858·81, and 2708·18 may still be regarded as lines, at least pending a further investigation of the bands.

The possibility of confusion between lines and band-heads (which is liable to arise where the source is at a low pressure and the band-heads are only faintly recorded on the plate) was perhaps not so well known at the time of Schniederjost's work as it is now. The modification of intensities in the line-structure of a band as observed under some conditions is often such that a band-head resembles a line winged on one side *.

Finally, it may be noted that this communication is concerned only with the O.I observations of Schniederjost, and has no reference to the O.II lines † (of the "elementary line" spectrum) measured by him. The latter have, in the main, been confirmed and amplified by Professor Fowler.

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* For a plate illustrating this effect in silicon nitride bands, for instance, see: W. Jevons, Roy. Soc. Proc., A, lxxxix. plate 9, p. 193 (1913).

† *Loc. cit.* p. 283 ; see also Kayser's *Handbuch*, vi. p. 218.

LIII *On the Helmholtz Theories of the Struck String.*—
Part I. *Theoretical. By* W. H. GEORGE, *B.Sc., Research
Student, University College, Nottingham* *.

[Plate III.]

SUMMARY.—The various theoretical treatments of the struck
string are noted, and the Helmholtz theory for the hard hammer
is then considered in detail, and is shown to be in conflict with
experimental evidence. The Helmholtz theory for the elastic
hammer is next considered, with the omission of two assumptions
which caused Kaufmann to reject the theory. Expressions are
found for quantities whose magnitude can be determined from
photographically obtained displacement-time curves of the struck
point. Expressions for the same quantities are derived from
Kaufmann's theory of the string struck at the mid-point, and also
from Kaufmann's approximate theory of the string struck near
one end. The comparison of the theoretically and experimentally
determined quantities is to be given in the second part of the
paper.

INTRODUCTION.

THE problem of the struck string has been theoretically
treated by two methods. Helmholtz †, Delemer ‡,
and Lamb § each assume some special form for the pressure
between the hammer and the string during the time of
contact. Proceeding from the assumed pressure-time laws
and using some additional assumptions, each of these writers
obtains finally an expression giving the intensities of the
partials of the freely vibrating string. None of these treat-
ments which illustrate the first method appears to have been
subjected to quantitative experimental tests.

The second method of treatment is that due to Kaufmann ‖,
who considers the problem of the impact of a massive *un-
yielding* particle on the string. He gives a rigorous treat-
ment for the string of infinite length, and also for the finite
string struck at the middle point, provided, in this second
case, that the time of contact between hammer and string is
not greater than the fundamental free period of the string.
In an attempt to simplify the work, he treats the case of the

present paper. There are no other recorded experiments in which any device for withdrawing the hammer has been used.

We may therefore conclude that this theory is inapplicable to the experimental results so far published.

Helmholtz's Theory for the Elastic Hammer.

In order to treat the problem of a string struck with a felt - covered hammer, Helmholtz (*loc. cit.* Appendix v.) observed that " the elastic pad yields to the blow at first and then recovers itself, so that while the hammer is in contact with the string, the motion is capable of extending over a considerable length . . . . . Observing that the string moves but very slightly from its position of rest, and that the elastic pad of the hammer is very yielding and admits of much compression, we may simplify the mathematical theory, by assuming the pressure exerted by the hammer during the blow which it gives to the string to be $P = A \sin \pi t/\tau$," where $t =$ variable time, $\tau =$ duration of contact, and A is a constant which may be seen to be the value of the pressure when $t = \tau/2$. With the aid of an additional assumption as to the time of contact, Helmholtz obtains finally an expression giving the amplitude of the partials in the tone of the freely vibrating string.

Kaufmann rejected this theory because he concluded that (i.) the elasticity of the hammer is a negligible factor compared with the tension of the string in causing the rebound of the hammer, and (ii.) $(\tau/\theta) > (a/l)$ whilst Helmholtz had *assumed* that $(\tau/\theta) < (a/l)$. It is clear, however, that the original assumption of the pressure law is not explicitly dependent on either of these two assumptions, and the purpose of the remainder of the present paper is a reconsideration of this Helmholtz theory, with the omission of the two assumptions which are in conflict with Kaufmann's experimental work. Since the displacement-time curve of the struck point can be so conveniently obtained by the photographic method due to A. Rafs and Ö. Krigar-Menzel [*], we proceed to derive from the Helmholtz pressure law expressions for quantities whose magnitude can be readily determined from such a curve.

* A. Rafs and O. Krigar-Menzel, Wied. *Ann.* vol. xliv. p. 623 (1891).

Theory.

Notation :—

    l = length of string (in cm.).

    a = distance of struck point from nearer bridge (in cm.).

    b = distance of struck point from farther bridge (in cm.).

    y = variable displacement of struck point reckoned positive in the direction of the approaching hammer (in cm.).

    y_1 = displacement of struck point at the instant of separation of hammer and string (in cm.).

    y_2 = maximum displacement of struck point (in cm.).

    r = distance between string and axis of rotation of hammer (in cm.).

    θ = free period of fundamental tone of string (in sec.).

    τ = duration of impact (in sec.).

    t = variable time reckoned from the instant of the beginning of the impact (in sec.).

    t_2 = time taken for y to reach its maximum value (in sec.).

    v_0 = initial velocity of hammer (in cm. per sec.).

    v = velocity of hammer at instant of separation of hammer and string (in cm. per sec.).

    μ = linear density of string (in gm. per cm.).

    m = mass of hammer (see following note).

    M = mass of string = μl (in gm.).

The actual hammer under consideration may be regarded as a compound pendulum. By the term "*mass of hammer*" is meant the mass in gm. of a particle equimomental with the hammer and distant r from the axis of rotation of the pendulum; that is, the moment of inertia of the pendulum about its axis of rotation is mr^2. We assume that the motion takes place in one plane passing through the string. For the force on the hammer we may write

$$m\frac{d^2y}{dt^2} = -\mathrm{A}\sin\frac{\pi t}{\tau}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$(0 < t < \tau)$$

Hence

$$\int_{v_0}^{\frac{dy}{dt}} d\left(\frac{dy}{dt}\right) = -\frac{\mathrm{A}}{m}\int_0^t \sin\frac{\pi t}{\tau} . \, dt.$$

It will be noted that we have put $dy/dt = v_0$ when $t = 0$. If this be regarded as an assumption, it can be seen to be clearly justifiable by an examination of the experimentally

obtained displacement-time curves accompanying this paper. Integrating, we have

$$\frac{dy}{dt} = v_0 + \frac{A}{m} \cdot \frac{\tau}{\pi} \left(\cos \frac{\pi t}{\tau} - 1 \right). \quad . \quad . \quad . \quad (2)$$
$$(0 < t < \tau)$$

By putting $t = \tau/2$ in equation (1), we see that the Helmholtz constant A is the value of the force exerted by the hammer on the string when $t = \tau/2$. As this quantity is not readily determined by experiment, we may eliminate it from the equations by introducing a new quantity—the velocity of rebound (v) of the hammer which has not hitherto been considered in the study of the struck string. It may be noted in passing that the writer hopes to study the energy aspect of the general problem by the aid of this quantity, since in the ideal case the energy absorbed by the vibrating system is $\frac{1}{2}m(v_0^2 - r^2)$. By putting $t = \tau$ in equation (2), we find

$$v = v_0 - \frac{2A\tau}{\pi m}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or
$$A = \frac{m\pi}{2\tau}(v_0 - v) . \quad . \quad . \quad . \quad . \quad (3a)$$

Hence equation (2) may be rewritten thus :

$$\frac{dy}{dt} = \frac{1}{2} \left[(v_0 + v) + (v_0 - v) \cos \frac{\pi t}{\tau} \right]. \quad . \quad . \quad (2a)$$
$$(0 < t < \tau)$$

Integrating again and putting in the condition that $y = 0$ when $t = 0$, we have

$$y = \frac{1}{2} \left[(v_0 + v)t + \frac{\tau}{\pi}(v_0 - v) \sin \frac{\pi t}{\tau} \right]. \quad . \quad . \quad (4)$$
$$(0 < t < \tau)$$

By putting $t = \tau$ in this equation, we see that the displacement of the struck point at the instant of separation of hammer and string is given by

$$y_1 = \frac{\tau}{2}(v_0 + v). \quad . \quad . \quad . \quad . \quad . \quad (5)$$

When the string under considerable tension is struck by a light hammer near one of the bridges, the actual displacements of the struck point are so small that it is almost useless to attempt to measure any but the maximum value

(y_2) of the displacement. Observing that the hammer is then instantaneously at rest, we obtain the time (t_2) for y to reach its maximum value from equation (2 a) by putting $dy/dt = 0$. Hence

$$t_2 = \frac{\tau}{\pi} \left\{ \pi - \cos^{-1}\left(\frac{v_0 + v}{v_0 - v}\right) \right\} \quad . \quad . \quad . \quad (6)$$

Putting this value in equation (4), we obtain

$$y_2 = \frac{\tau}{2\pi} \left\{ (v_0 + v)\left[\pi - \cos^{-1}\left(\frac{v_0 + v}{v_0 - v}\right) \right] + 2\sqrt{-vv_0} \right\}. \quad (7)$$

By use of a planimeter the area between the curve and the axis of time may be conveniently measured, and is given by

$$\int_0^t y\, dt = \frac{1}{2}\left[\frac{1}{2}(v_0 + v)t^2 + \frac{\tau^2}{\pi^2}(v_0 - v)\left(\cos\frac{\pi t}{\tau} - 1\right) \right]. \quad (8)$$

In the special case when t reaches its maximum value of τ, we have

$$\int_0^\tau y\, dt = \tau^2 \left[\frac{1}{4}(v_0 + v) + \frac{1}{\pi^2}(v_0 - v) \right]. \quad . \quad . \quad (9)$$

We proceed to compare these results with those derived from Kaufmann's theory.

Comparison with Kaufmann's Theory for a String struck at the Mid-Point.

The Kaufmann equations [*] for this case, which, it may be noted, hold only if the time of contact is less than one period of the string, run as follows:—

$$y = v_0 \theta \frac{m}{4M}\left(1 - e^{-\frac{4M}{m}\cdot\frac{t}{\theta}}\right), \quad . \quad . \quad . \quad (10)$$
$$\left(0 < \frac{t}{\theta} < \frac{1}{2}\right)$$

$$y = v_0 \theta \left\{ e^{-\frac{4M}{m}\cdot\frac{t}{\theta}}\left[2e^{\frac{2M}{m}}\left(\frac{t}{\theta} - \frac{1}{2} + \frac{m}{4M}\right) - \frac{m}{4M} \right] - \frac{m}{4M} \right\},$$
$$\left(\frac{1}{2} < \frac{t}{\theta} < 1\right) \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad . \quad . \quad . \quad (11)$$

$$\frac{\tau}{\theta} = \frac{1}{2} + \frac{1}{4}\frac{m}{M}\left(1 + \frac{1}{2}e^{-\frac{2M}{m}}\right). \quad . \quad . \quad (12)$$

---

[*] There are some printer's errors on p. 688 of Kaufmann's paper, and both forms of the final equation are given wrongly. Equation (11), as here given, will be found to agree with Kaufmann's own numerical calculations.

Differentiating (10) and (11) each once with respect to time, we obtain

$$\frac{dy}{dt} = v_0 e^{-\frac{4M}{m} \cdot \frac{t}{\theta}}, \quad \quad \quad \quad (13)$$

$$\left(0 < \frac{t}{\theta} < \frac{1}{2} \right)$$

$$\frac{dy}{dt} = v_0 e^{-\frac{4M}{m} \cdot \frac{t}{\theta}} \left\{ -\frac{4M}{m} \left[2e^{\frac{2M}{m}} \left(\frac{t}{\theta} - \frac{1}{2} + \frac{m}{4M} \right) - \frac{m}{4M} \right] \right.$$

$$\left(\frac{1}{2} < \frac{t}{\theta} < 1 \right) \quad \quad \quad \quad \left. + 2e^{\frac{2M}{m}} \right\} \cdot \quad (14)$$

Combining equations (14) and (12), we obtain the velocity of rebound of the hammer :

$$v = -2v_0 e^{-\left(1 + \frac{1}{2} e^{-\frac{2M}{m}} \right)}. \quad \quad \quad (15)$$

The pressure law can be derived from equations (13) and (14) by differentiating each once more with respect to time and then multiplying by the mass of the hammer :

$$m\frac{d^2y}{dt^2} = -v_0 \frac{4M}{\theta} e^{-\frac{4M}{m} \cdot \frac{t}{\theta}}, \quad \quad \quad (16)$$

$$\left(0 < \frac{t}{\theta} < \frac{1}{2} \right)$$

$$m\frac{d^2y}{dt^2} = -v_0 \frac{8M}{\theta} e^{\frac{2M}{m} \left(1 - \frac{2t}{\theta} \right)} - v_0 \frac{4M}{\theta} e^{-\frac{4M}{m} \cdot \frac{t}{\theta}} \left\{ -\frac{4M}{m} \times \right.$$

$$\left(\frac{1}{2} < \frac{t}{\theta} < 1 \right) \quad \left[2e^{\frac{2M}{m}} \left(\frac{t}{\theta} - \frac{1}{2} + \frac{m}{4M} \right) - \frac{m}{4M} \right] + 2e^{\frac{2M}{m}} \right\}. \quad (17)$$

The displacement (y_1) of the struck point at the instant of separation of hammer and string is found from equations (11) and (12) to be

$$y_1 = v_0 \theta \frac{m}{M} \left[e^{-\left(1 + \frac{1}{2} e^{-\frac{2M}{m}} \right)} - \frac{1}{4} \right]. \quad \quad (18)$$

The time taken for y to reach its maximum value (y_2) is found by equating the right-hand side of equation (14) to zero. Whence

$$t_2 = \frac{\theta}{2} \left(1 + \frac{1}{4} \frac{m}{M} e^{-\frac{2M}{m}} \right). \quad \quad \quad (19)$$

Hence

$$y_2 = \frac{v_0 \theta m}{4M} \left\{ 2e^{\left(-\frac{1}{2} e^{-\frac{2M}{m}} \right)} - 1 \right\}. \quad \quad (20)$$

The area contained between the curve and the axis of time is the sum of two parts which have to be determined separately from equations (10) and (11). We have from equation (10)

$$\int_0^t y \, dt = v_0 \theta \frac{m}{4M} \left(\int_0^t dt - \int_0^t e^{-\frac{4M}{m} \cdot \frac{t}{\theta}} dt \right)$$

$$\left(0 < \frac{t}{\theta} < \frac{1}{2} \right) \qquad = v_0 \theta \frac{m}{4M} \left[t + \frac{\theta m}{4M} \left(e^{-\frac{4M}{m} \cdot \frac{t}{\theta}} - 1 \right) \right], \quad (21)$$

and from equation (11)

$$\int_{\frac{\theta}{2}}^t y \, dt = v_0 \theta \left\{ \frac{2}{\theta} e^{\frac{2M}{m}} \int_{\frac{\theta}{2}}^t t \, e^{-\frac{4M}{m} \cdot \frac{t}{\theta}} dt + \left[e^{\frac{2M}{m}} \left(\frac{m}{2M} - 1 \right) \right. \right.$$

$$\left(\frac{1}{2} < \frac{t}{\theta} < 1 \right) \qquad \left. - \frac{m}{4M} \right] \int_{\frac{\theta}{2}}^t e^{-\frac{4M}{m} \cdot \frac{t}{\theta}} \cdot dt - \frac{m}{4M} \int_{\frac{\theta}{2}}^t dt \right\}$$

$$= v_0 \theta \left\{ \frac{\theta}{8} \cdot \frac{m^2}{M^2} e^{\frac{2M}{m}} \left[e^{-\frac{2M}{m}} \left(\frac{2M}{m} + 1 \right) - e^{-\frac{4M}{m} \cdot \frac{t}{\theta}} \left(\frac{4M}{m} \cdot \frac{t}{\theta} + 1 \right) \right] \right\}$$

$$+ v_0 \theta \left\{ \left[e^{\frac{2M}{m}} \left(\frac{m}{2M} - 1 \right) - \frac{m}{4M} \right] \left(e^{-\frac{2M}{m}} - e^{-\frac{4M}{m} \cdot \frac{t}{\theta}} \right) \frac{m\theta}{4M} \right.$$

$$\left. - \frac{m}{4M} \left(t - \frac{\theta}{2} \right) \right\} \quad . \quad . \quad . \quad (22)$$

Fig. 1.
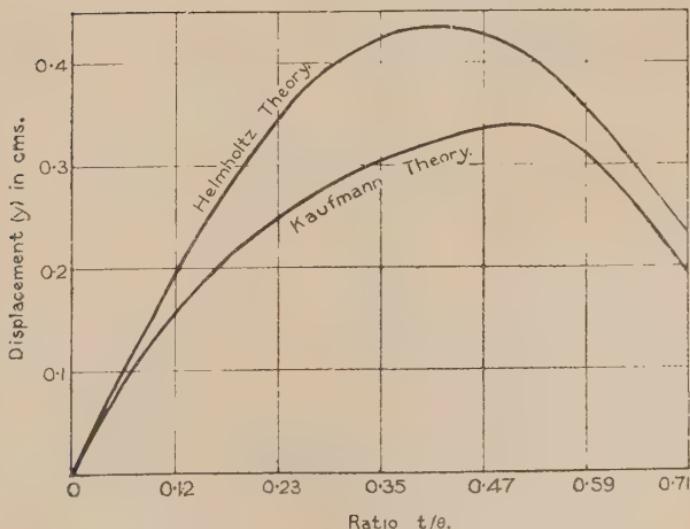
Theoretical displacement-time curves for the struck point.
$M = 4\cdot8$; $m = 4\cdot4$; $\theta = 1/128$; $\tau\theta = 0\cdot74$; $v_0 = 215$; $v = -149$; $l/a = 2$.

COMPARISON WITH KAUFMANN'S THEORY FOR A STRING
STRUCK NEAR ONE END.

Kaufmann's equations for this case run thus :—

$$\underset{\left(0<\frac{t}{\theta}<\frac{b}{l}\right)}{y} = \frac{v_0\theta}{\sqrt{\dfrac{M}{m_0}\left(4\dfrac{l}{a}-\dfrac{M}{m_0}\right)}}\, e^{-\frac{M}{m_0}\cdot\frac{t}{\theta}}$$
$$\times \sin\left\{\frac{t}{\theta}\sqrt{\frac{M}{m_0}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}\right\}, \quad . \quad (23)$$

and

$$\underset{\left(\frac{\tau}{\theta}=\frac{b}{l}\right)}{\frac{\tau}{\theta}} = \frac{1}{\sqrt{\dfrac{M}{m_0}\left(4\dfrac{l}{a}-\dfrac{M}{m_0}\right)}}\tan^{-1}\left\{\frac{\sqrt{\dfrac{M}{m_0}\left(4\dfrac{l}{a}-\dfrac{M}{m_0}\right)}}{-2\dfrac{l}{a}+\dfrac{M}{m_0}}\right\} \quad (24)$$

The approximations used by Kaufmann have already been noted in the introduction to this paper, and the quantity m_0 is defined thus: $m_0 = m + \mu a/3$—that is, to the mass of the hammer (m) is added the mass of a particle which, if placed on the struck point, would be equimomental with the shorter piece of string (of length a) so far as rotations about the nearer bridge are concerned. It will be recalled that Kaufmann assumes that this shorter piece of the string remains uncurved during the period of impact.

We proceed, as before, to derive from these equations the special quantities required.

At the instant of separation of hammer and string we have

$$y_{\mathrm{I}} = \frac{a}{2l}v_0\,\theta\, e^{-\frac{M}{m_0}\cdot\frac{1}{\sqrt{\frac{M}{m_0}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}}\tan^{-1}}\left\{\frac{\sqrt{\dfrac{M}{m_0}\left(4\dfrac{l}{a}-\dfrac{M}{m_0}\right)}}{-2\dfrac{l}{a}+\dfrac{M}{m_0}}\right\} \quad (25)$$

From equation (23) we have

$$\underset{\left(0<\frac{t}{\theta}<\frac{b}{l}\right)}{\frac{dy}{dt}} = \frac{v_0 e^{-\frac{M}{m_0}\cdot\frac{t}{\theta}}}{\sqrt{\dfrac{M}{m_0}\left(4\dfrac{l}{a}-\dfrac{M}{m_0}\right)}}\cdot\left\{\sqrt{\frac{M}{m_0}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}\right.$$
$$\times \cos\left[\frac{t}{\theta}\sqrt{\frac{M}{m_0}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}\right]$$
$$\left.-\frac{M}{m_0}\sin\left[\frac{t}{\theta}\sqrt{\frac{M}{m_0}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}\right]\right\} \quad . \quad . \quad (26)$$

Hence the velocity of rebound is given by

$$v = -v_0 e^{-\frac{M}{m_0} \cdot \frac{1}{\sqrt{\frac{M}{m_0}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}} \tan^{-1}\left\{\frac{\sqrt{\frac{M}{m_0}}\left(\frac{l}{a}-\frac{M}{m_0}\right)}{-2\frac{l}{a}+\frac{M}{m_0}}\right\}} . \quad (27)$$

The time (t_2) taken for y to reach its maximum value is found from equation (26) to be

$$t_2 = \frac{\theta}{\sqrt{\frac{M}{m_0}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}} \tan^{-1}\left[\frac{m_0}{M}\sqrt{\frac{M}{m_0}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}\right]. \quad (28)$$

Hence the maximum displacement (y_2) of the struck point is given by

$$y_2 = v_0\theta\sqrt{\frac{1}{4}\frac{a}{l}\frac{m_0}{M}} \cdot e^{-\frac{M}{m_0} \cdot \frac{1}{\sqrt{\frac{M}{m_0}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}} \tan^{-1}\left(\sqrt{\frac{m_0}{M}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}\right)} \quad . \quad . \quad . \quad (29)$$

The pressure law is obtained from equation (26) :

$$m_0\frac{d^2y}{dt^2} = \frac{2Mv_0 e^{-\frac{M}{m_0}\cdot\frac{t}{\theta}}}{\theta\sqrt{\frac{M}{m_0}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}}\left\{\left(\frac{M}{m_0}-\frac{2l}{a}\right)\right.$$

$$\times \sin\left[\frac{t}{\theta}\sqrt{\frac{M}{m_0}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}\right] - \sqrt{\frac{M}{m_0}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}$$

$$\left.\times \cos\left[\frac{t}{\theta}\sqrt{\frac{M}{m_0}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}\right]\right\}. \quad . \quad . \quad . \quad (30)$$

Finally the area between the curve and the axis of time is found from equation (23) by integrating by parts and solving for the desired integral, whence

$$\int_0^t y\, dt = \frac{v_0}{\sqrt{\frac{M}{m_0}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}}\frac{\theta^2 a m_0}{4lM}\left\{\sqrt{\frac{M}{m_0}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}\right.$$

$$\left(0 < \frac{t}{\theta} < \frac{b}{l}\right)$$

$$-e^{-\frac{Mt}{m_0\theta}}\left[\frac{M}{m_0}\sin\left\{\frac{t}{\theta}\sqrt{\frac{M}{m_0}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}\right\}\right.$$

$$\left.\left.+\sqrt{\frac{M}{m_0}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}\cos\left\{\frac{t}{\theta}\sqrt{\frac{M}{m_0}\left(4\frac{l}{a}-\frac{M}{m_0}\right)}\right\}\right]\right\}. \quad (31)$$

The comparison of the theoretically and experimentally determined quantities will be given in the second part of the paper.

Fig. 2.
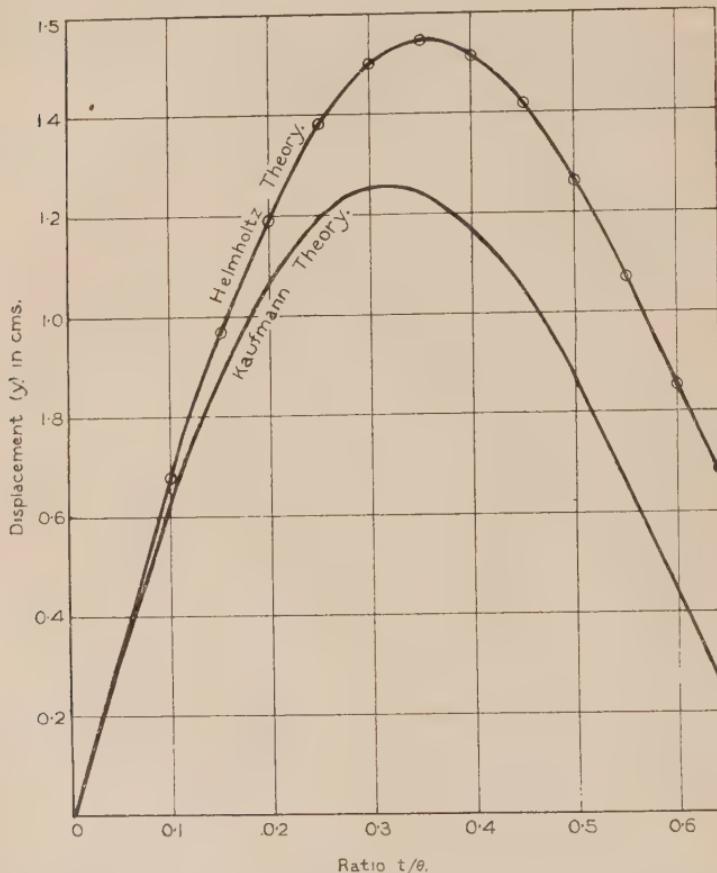
Theoretical displacement-time curves for the struck point.
$M = 29\cdot4$; $m = 49\cdot5$; $m_0 = 50\cdot6$; $\theta = 1/47$; $\tau/\theta = 0\cdot64$; $v_0 = 325$;
$v = -224$; $l/a = 9$.

The writer wishes to thank the Council of the University College, Nottingham, and the Department of Scientific and Industrial Research for research grants; Prof. E. H. Barton, F.R.S., for his sympathetic interest in the work; Mr. F. Underwood, B.Sc., for kindly verifying the mathematics.

University College, Nottingham,
    Dec. 1923.

FIG. 1.
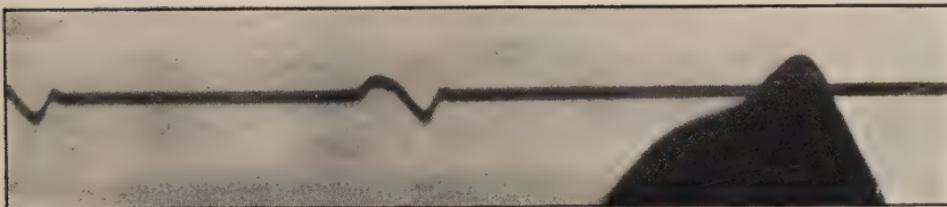
Experimental Displacement-Time Curve. Wedge-shaped metallic hammer.
$m/M = 0.27$; $l/a = 26$.

FIG. 2.
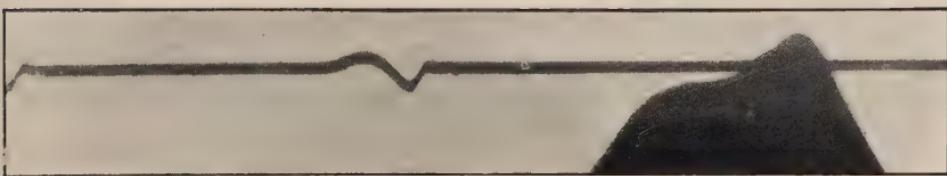
Experimental Displacement-Time Curve. Broad felt-covered hammer.
$m/M = 0.27$; $l/a = 26$.

FIG. 3.

FIG. 4.

LIV. *The Potential Gradient in the Sodium-Potassium Vapour Arc Lamp. By* F. H. NEWMAN, *D.Sc., A.R.C.S., Professor of Physics, University College, Exeter* *.

1. *Introduction.*

A SODIUM-POTASSIUM vapour arc lamp similar in principle to the more familiar mercury vapour lamp has been previously described by the author †. This lamp works with a relatively small applied potential difference,— the arc can be struck with 30 volts,—and when once the arc has been started the fall of potential between the terminals is only 10 volts with a current of 1·5 amp. This potential difference is very small when compared with the carbon arc, and is less than that required to operate the mercury arc except the low voltage arc in mercury vapour, which acts on a different principle.

The relative intensity of the potassium and sodium lines emitted when the alloy lamp is working varies in different parts of the tube. The potassium lines are brightest near the anode. At the cathode the subordinate lines of sodium are the most intense.

The theoretical value of the resonance potential of sodium vapour is 2·10 volts, and electrons of this energy produce the D lines. Electrons having a velocity corresponding to 5·13 volts are able to ionize sodium vapour and cause it to emit all the lines, including those of the subordinate series. The resonance potential of potassium vapour is 1·60 volts, while the ionization potential is 4·33 volts. In a mixture of sodium and potassium vapours, as the accelerating potential is increased the 7699, 7665 doublet of potassium should appear first, then the 5896, 5890 doublet of sodium, followed by the subordinate series lines of potassium and sodium respectively. It would thus appear that as the potassium lines are brightest near the anode of the lamp, the fall of potential at this terminal is less than at the cathode. Low voltage arcs in metallic vapours suggest that it is possible to eject the electron to infinity from the $2p$ ring, for these arcs operate at a potential below the ionization potential. The energy necessary to eject the electron from this orbit will certainly be less than that required if the electron is in the 1·5 S orbit. The transfer to the $2p$ ring may be obtained by

means of the energy obtained from the bombardment by electrons having energy equal to the resonance potential, or by the absorption of radiation $h\nu$ from adjacent atoms which are in the partially ionized condition. Atoms of metallic vapours seem to permit of the radiant energy, liberated by each electron impact which results in radiation, to be passed on from atom to atom, and this multiplies the fraction of atoms which are in the abnormal or partially ionized condition. The greater part of the radiation emitted when the electrons fall from the $2p$ to the $1\cdot5\,S$ ring will escape from the tube, but some of it may be taken up by neighbouring atoms. This absorption effect will increase with the vapour pressure, and with an increase in the density of the bombarding electrons. In the alloy vapour lamp the conditions are such that the ionization is produced mainly by this " cumulative action."

When the electrical discharge passes through gases at low pressure the cathode and anode falls of potential depend on the nature of the electrodes, and they fall to comparatively low values for the strongly positive alkali metals. Mey[*] has shown that the alloy of sodium and potassium, used as the cathode, has a smaller cathode fall in most gases than that of any metal, so it is to be expected that the potential difference between the terminals in the alloy lamp would be small.

In the investigation of the distribution of electron force along the arc of the lamp the probe method was employed. The potential acquired by a platinum wire placed in various positions along the line of discharge was measured, and if it is assumed that the potential of the wire is the same as that of the vapour with which it is in contact, we get from these observations a means of determining the distribution of the electric force along the lamp. For such a method to be successful the secondary probe electrode must take up the potential of the vapour with which it is in contact. To enable it to do so there must be a plentiful supply of both positive and negative ions in the gas to give up their charges to the wire, and thus raise or lower the potential of the wire to equality with the surrounding vapour. In the arc discharge there is a copious supply of ions of both signs, so the assumption that the secondary electrode does acquire the potential of the vapour with which it is in contact seems to be justified.

[*] *Verh. Deutsch. Physik. Gesel.* v. p. 72 (1903).

2. *Experiments.*

The form of lamp used is shown in fig. 1. A quartz tube was bent to the shape shown in order that both electrodes should consist of the alloy,—two parts by weight of sodium, and one of potassium. Connexion was made with these

. Fig. 1.
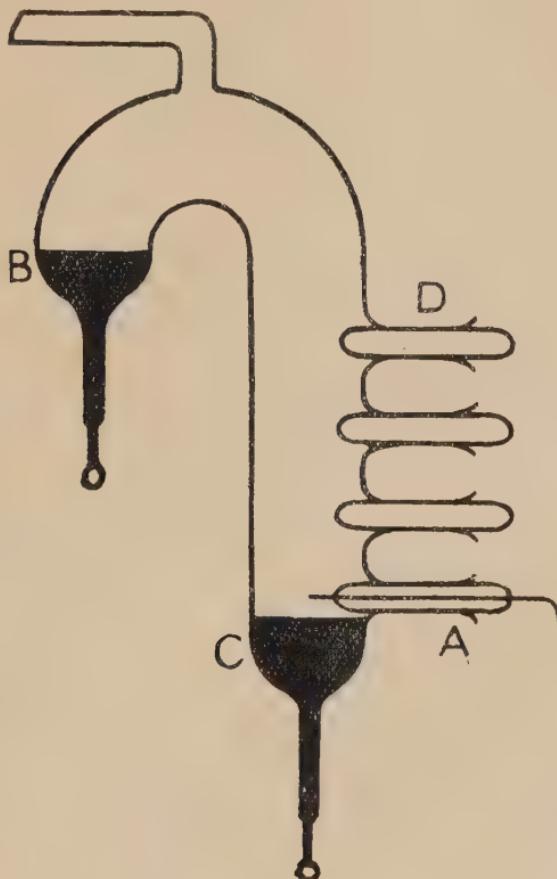
electrodes by aluminium wires sealed into the quartz with sealing-wax. Providing the current was not greater than 2 amps. the wax did not soften. The tube, which was about 10 cm. long and 1 cm. in diameter, had four side tubes each 3 cm. long for the insertion of the probe electrode. The latter consisted of a platinum wire sealed into a glass stopper with 3 mm. of wire protruding from the end inside the lamp.

As very little external heating is required to start the arc, the ends of these side tubes remained cool and so the vacuum was maintained. It was arranged that the platinum wire should reach the axis of the main tube. The alloy was introduced into the lamp at A, and after the apparatus had been well exhausted the surface of the alloy was made clear by passing an electrical discharge through the tube, the film of oxide disintegrating and dissolving in the alloy. By tilting the tube some of the alloy could then be run into the part B without fouling the length of the tube. The amount of alloy in C could be adjusted so that the surface was about 3 mm.—as measured by a cathetometer—from the probe electrode inserted at A. The total length measured along the axis of the lamp between the surfaces of the two alloy terminals was 8 cm.

The electrode C was connected to one pair of quadrants of a Dolezalek electrometer, and the probe electrode to the other pair of quadrants, the needle of the electrometer being maintained at 100 volts. The current through the lamp was kept constant by means of an adjustable resistance placed in series. It was found that with this shape of lamp the arc did not wander, and so the current remained constant once the temperature of the lamp reached a steady value. The arc was struck by connecting one terminal to a small induction coil and passing a momentary discharge, although sometimes the arc would strike automatically with an applied potential difference of 50 volts by slightly heating the cathode. The side tube D was situated rather more than half way along the lamp. At first C was made the cathode and the potential difference between it and the probe, inserted in the four side tubes, was determined. The current was then reversed and C was the anode. The potential difference between it and the four positions of the probe was again determined. In this way the uncertainty of obtaining correct measurements near B was avoided.

3. *Experimental Results.*

The results obtained for the potential gradient along the lamp are shown in Table I.

These results show that the potential gradient along the arc column is uniform, and therefore, as shown by Poisson's law $\frac{\delta^2 V}{\delta x^2} = -4\pi\rho$, there cannot be a preponderance of ions of one sign or the other in it. The cathode fall—3·8 volts—is

greater than the anode fall—2·5 volts,—but both are small
compared with the results for other metal electrodes.

TABLE 1.

Potential difference between terminals 12·0 volts.
Current in lamp 1·5 amp.

Distance from cathode.	Corresponding Potential.	Distance from anode.	Corresponding Potential.
cathode.	0 volts.	anode.	12·0 volts.
3 mm.	3·8 „	3 mm.	9·5 „
18 „	5·0 „	18 „	8·3 „
32 „	6·1 „	32 „	7·2 „
48 „	7·4 „	48 „	5·9 „

Unfortunately the current through the lamp cannot be in-
creased much more than 2 amp. as the heat developed causes a
brown deposit on the quartz to appear, and this interferes
with the steady working of the lamp. It was found, however,
that for currents between 1 and 2 amp. both the cathode and
anode falls of potential decreased slightly with increasing
current. This is probably due to the increase in the vapour
density.

The wave form of the current was investigated with
Duddell's permanent magnet type of oscillograph. The
vibrator was specially stretched so that it was able to follow
any variation in the current up to 500 per second. The
resulting curves were photographed by means of a falling
plate camera, the speed of the plate at the instant of
photographing being about 400 cm. per second. The vibrator,
in series with a high non-inductive resistance, was placed in
shunt with the main current. The resulting oscillograms
were straight lines showing that the current was very
steady. The potentials measured were therefore the actual
potentials at the different parts of the lamp and not average
potentials.

The small potential difference between the terminals of
the lamp when the arc is passing depends on the photo-
electric effect exhibited by the alloy. In a vacuum such as
is present in the lamp, the negative corpuscles are projected

with sufficient energy to make their way against a small retarding force. The electrons near the surface of the alloy ionize the vapour, even though the electric field is so weak that the kinetic energy given by it to the electrons is too small to make them act as ionizers. Warburg * has shown that the presence of minute traces of oxygen in gases such as hydrogen or nitrogen produces a great diminution in the current from a negative point, which seems to indicate that oxygen has a great tendency to collect round the carriers of the negative charge, and either makes them less efficient as ionizers, or else makes them move more slowly in the electric field. It is probable too that oxygen increases the difficulty of getting the electrons from the point into the gas, as Warburg has shown that the presence of a trace of oxygen produces a large increase in the cathode fall of potential in vacuum tubes. All traces of oxygen are of course removed in the lamp by the sodium-potassium alloy, and this fact causes the potential gradient along the lamp to be small.

The photoelectric effect produces the same effect, although in a smaller degree, as the emission of electrons from the incandescent filament in low voltage arcs. With such arcs it is always found that the striking potential difference is always greater than that required to maintain the arc, and this is so with the alloy vapour lamp.

4. *Summary.*

1. The potential gradient along the arc of a vapour lamp using the liquid alloy of sodium and potassium as terminals has been investigated.

2. The cathode fall of potential is greater than the anode fall, but both are small compared with results for other metal terminals. The potential gradient along the arc column is uniform.

3. The small potential difference between the terminals of the lamp when it is working is explained by the photo-electric effect exhibited by the alloy.

* *Ann. der Phys.* xi. p. 295 (1900).

LV. *On the Anomalous Behaviour of a Vibration Galvanometer. By* E. V. APPLETON, *M.A., D.Sc., Cavendish Laboratory, Cambridge* *.

THERE is in use in the Advanced Practical Physics class at the Cavendish Laboratory a vibration galvanometer which, for quantitative work, has been found to exhibit certain peculiarities in that one of two possible deflexions is obtainable for a single value of the current passing through the galvanometer coil. The particular deflexion obtained in any case is dependent on the method by which the current is made to approach its final value. From time to time students † in the class have been asked to investigate experimentally the relation between the amplitude of oscillation of the suspended system and the frequency and amplitude of the alternating current passing through the instrument. The present paper deals with some of the results of these investigations, to which I have added an approximate theoretical treatment which seems to account for the salient features of the phenomenon.

The instrument is of the Drysdale-Tinsley type, being in principle very similar to a Kelvin Mirror-galvanometer. The vibratory system is a suspension piece carrying a light mirror, to which is attached a small magnet of soft charcoal iron, the whole being suspended between the poles of a horse-shoe magnet. The natural period of the suspended system is controlled by means of a movable magnetic shunt on the permanent magnet. The exciting current passes through a fixed coil, the plane of which is parallel to the zero position of the suspended magnet.

If the position of the magnetic shunt is kept fixed, and thus the natural frequency of the suspended system kept constant, there are three variables to be considered, namely, the oscillatory amplitude A of the galvanometer, and the magnitude and angular frequency (I and p respectively) of the alternating current through the coil. Accordingly, the characteristic relations are given by plane curves showing the variation of the amplitude A with the current I for different values of the angular frequency p, or by curves

* Communicated by the Author.

† In this connexion I should like specially to mention Mr. R. W. Scholfield, of Trinity College, who was the first student to get a complete set of experimental results. His curves are reproduced in this paper.

showing the variation of amplitude with angular frequency for different values of constant current. The corresponding two sets of curves are illustrated in figures 1 and 2.

The data for the curves of fig. 1 were obtained by direct experiment, while those for fig. 2 were obtained indirectly from experimental values such as those exhibited in fig. 1.

Fig. 1.
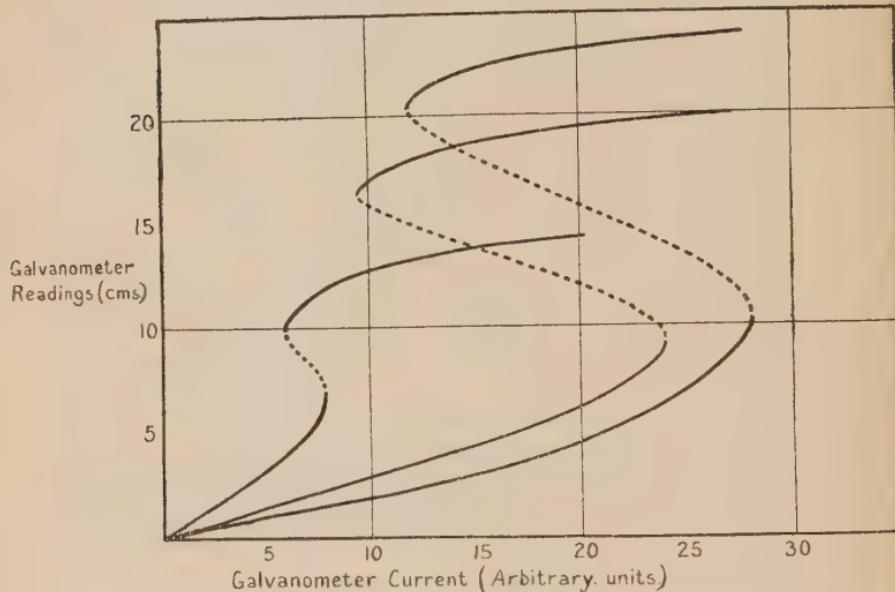
Showing relation between galvanometer current and galvanometer deflexion for different values of impressed frequency.

In obtaining the relation between the galvanometer deflexion and galvanometer current for a fixed impressed frequency cases of oscillation-hysteresis were obtained. This phenomenon is illustrated by the hysteresis loops in the curves in fig. 1. A typical example of this is redrawn in fig. 3.

In obtaining the data for this type of curve the current in the galvanometer circuit was introduced from an alternating-current source by means of a small air-core transformer with variable coupling, so that the galvanometer-current amplitude was continuously variable. On increasing the current amplitude from zero the galvanometer deflexion increased until conditions represented by the point F were reached, when the deflexion suddenly increased to the value indicated by B. For further increase of current the representative point of the diagram moved along the curve BC. On now reducing the current, the larger deflexion indicated by BD

Fig. 2.

Galvo Deflection (cms)

Frequency of Alternating Current.
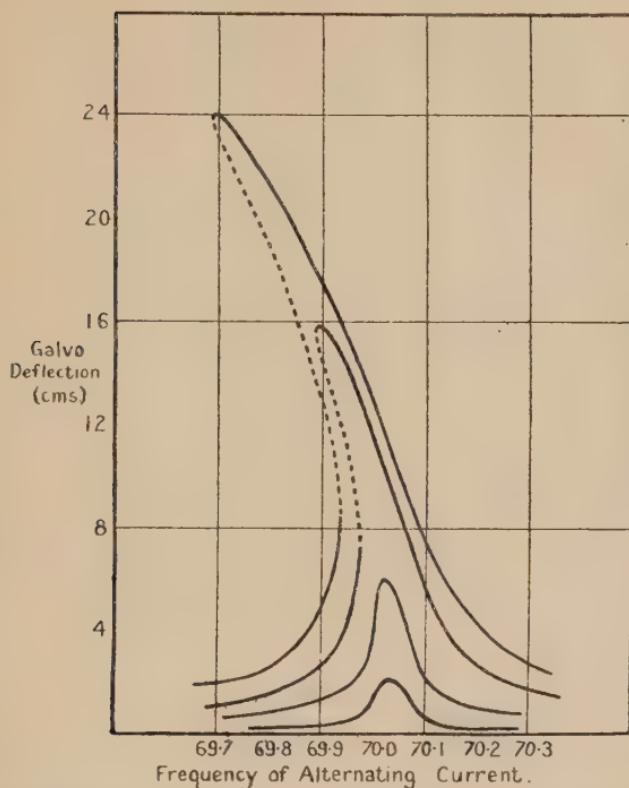
Showing relation between impressed frequency and galvanometer deflexion for different values of galvanometer current.

Fig. 3.

Galvanometer Deflection

Galvanometer Current.
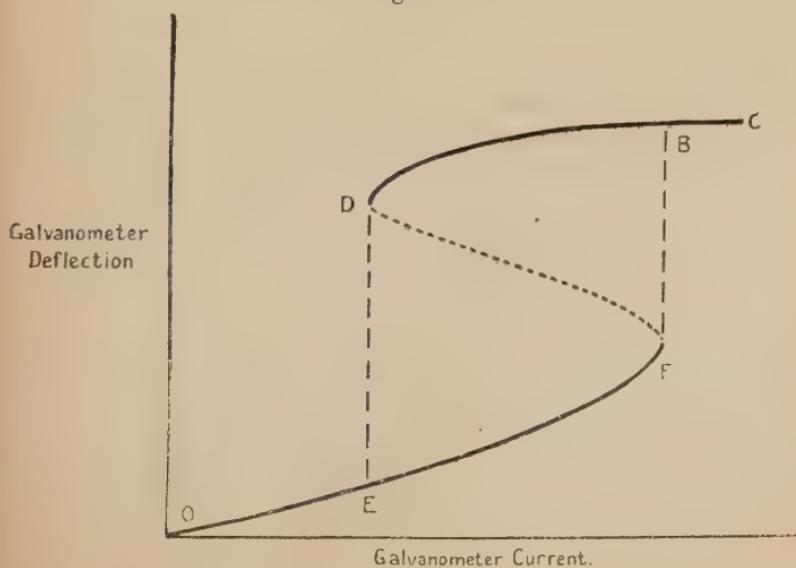
was maintained, until at conditions represented by D the amplitude suddenly fell to the lower value indicated by E. In other words, when the galvanometer current was increased from zero and then decreased again, the representative point traced the path OEFBCBDEO in fig. 3.

Between the two stable values of the galvanometer amplitude indicated by EF and DB there is a kind of "threshold" amplitude indicated by the broken line DF. Its physical existence is not easily realized, but I have found the following method useful in explaining the matter to students. Let us suppose that the galvanometer is maintaining the higher amplitude indicated by a point on DB when the galvanometer circuit is opened for a moment, cutting off the current supply. The amplitude falls rapidly, but if the circuit is quickly closed again the original amplitude is finally regained. If, however, the experiment is repeated, and the circuit is kept open long enough to allow the amplitude to fall just below the critical value indicated by the appropriate point on DF, the final amplitude attained, when the current flows again, is that indicated by a point on EF. After a few trials the appropriate amplitudes for the critical "threshold" values of DF may be approximately obtained in this way.

It is obvious from the curve of fig. 3 that for the region in which oscillation-hysteresis is found there are three possible oscillatory amplitudes of the suspended system of the galvanometer for one value of the current through the coil. Two of these amplitudes (represented by DB and EF) are stable, while the intermediate value (represented by DF) is unstable. It is also clear that this phenomenon is due, in some way, to the existence of some non-linear property or properties in the galvanometer system, but it is not obvious from figs. 1 & 3 whether such non-linearity is to be assumed in the terms representing the frictional and damping forces or in the terms associated with the restitution forces. The resonance curves of fig. 2, however, immediately suggest an alteration of the natural frequency of the galvanometer system with amplitude, and one is thus led to try to explain the phenomenon as a case of forced vibrations in an oscillatory system, the restoring force of which is not proportional to the displacement. A consideration of the design of the galvanometer shows that such non-linear forces are certainly to be expected. In this connexion there are three possible effects which tend to destroy the proportionality between

restoring couple and deflexion. These may be enumerated as follows :—

(1) The pole-strength of the soft-iron magnet will not be independent of amplitude, but will decrease with increasing amplitude. Apart from hysteresis, its magnitude will be proportional to $\cos \theta$, where θ is the angle of deflexion *.

(2) The restoring couple, apart from the inconstancy of pole-strength, will be proportional to $\sin \theta$ and not to θ.

(3) Since the pole-pieces of the permanent magnet are not very large, the magnetic field is most probably not homogeneous, being weaker at the sides of the gap than in the middle.

All of these effects act in the same way—that is to say, they tend to make the restoring force proportionally smaller the larger the angular deflexion. Bearing this in mind, we are at once led to suggest as a first approximation for the equation of motion of the suspension

$$K \frac{d^2\theta}{dt^2} + \left(A + \frac{B}{R}\right)\frac{d\theta}{dt} + c\theta(1 - \lambda\theta^2) = GI, \quad . \quad . \quad (1)$$

where

> K is the moment of inertia of the suspended system,
> R the resistance of the galvanometer and circuit,
> c the restoring couple per unit (small) angular displacement,
> I the current through the galvanometer coil,
> t the time,

and A, B, G, and λ are constants depending on the size and dimensions of the suspension, and on the magnitude and configuration of the magnetic field. For the experiment we are considering, I is sinusoidal ($I = I_0 \sin pt$), while R is constant. We may therefore write (1) as

$$\frac{d^2\theta}{dt^2} + 2\kappa \frac{d\theta}{dt} + \omega^2\theta(1 - \lambda\theta^2) = E\omega^2 \sin pt, \quad . \quad . \quad (2)$$

where

$$2\kappa = \frac{A}{K} + \frac{B}{RK}, \quad \frac{c}{K} = \omega^2, \quad \text{and} \quad E\omega^2 = \frac{GI_0}{K}.$$

* It may here be noted that the variation of the pole-strength with amplitude will have an effect on the "frictional" terms, in that the electromagnetic damping will not be strictly proportional to the angular velocity of the system.

Equation (2) will therefore be taken as the representative differential equation of motion of the galvanometer suspension, and we now proceed with its approximate solution.

Since we are interested only in the final amplitude of the forced vibration, we may neglect the transient terms representing the free vibration and adopt as a trial solution

$$\theta = a \sin pt + b \cos pt, \quad . \quad . \quad . \quad . \quad (3)$$

where a and b are unknown functions of the time. From the physical nature of the problem we may expect the growth or decay of the amplitude to vary slowly compared with the oscillation itself. In other words, we may assume that

$$\frac{da}{dt} << pa$$

and

$$\frac{db}{dt} << pb.$$

Hence the second differential coefficients of a and b with respect to time will be neglected. We thus have

$$\frac{d\theta}{dt} = \frac{da}{dt} \sin pt + ap \cos pt + \frac{db}{dt} \cos pt - bp \sin pt, \quad . \quad (4)$$

and

$$\frac{d^2\theta}{dt^2} = 2\frac{da}{dt} p \cos pt - ap^2 \sin pt - 2\frac{db}{dt} p \sin pt - bp^2 \cos pt. \quad (5)$$

In considering the non-linear term involving θ^3 we may, as a first approximation, neglect the influence of the harmonics on the fundamental and retain only those terms involving the angular frequency p. We thus have

$$\theta^3 = \tfrac{3}{4}a^3 \sin pt + \tfrac{3}{4}a^2 b \cos pt + \tfrac{3}{4}ab^2 \sin pt + \tfrac{3}{4}b^3 \cos pt. \quad . \quad (6)$$

On substituting for $\dfrac{d\theta}{dt}$, $\dfrac{d^2\theta}{dt^2}$, and θ^3 from (4), (5), and (6) in (2) and equating separately the terms involving $\sin pt$ and $\cos pt$, we have

$$\left.\begin{array}{l} 2\kappa\dfrac{da}{dt} - 2p\dfrac{db}{dt} + a(\omega^2 - p^2) - 2\kappa pb - \tfrac{3}{4}\omega^2\lambda a(a^2 + b^2) = \mathbf{E}\omega^2, \\[2mm] 2\kappa\dfrac{db}{dt} + 2p\dfrac{da}{dt} + b(\omega^2 - p^2) + 2\kappa pa - \tfrac{3}{4}\omega^2\lambda b(a^2 + b^2) = 0. \end{array}\right\}$$
$$. \quad . \quad . \quad . \quad (7)$$

But for stationary conditions, when a and b are constant, (7) becomes

$$\left.\begin{array}{c}(\omega^2 - p^2)a - 2\kappa pb - \tfrac{3}{4}\omega^2\lambda a(a^2 + b^2) = E\omega^2, \\ (\omega^2 - p^2)b + 2\kappa pa - \tfrac{3}{4}\omega^2\lambda b(a^2 + b^2) = 0. \end{array}\right\} \quad (8)$$

Let us now make the substitutions

$$\frac{p}{\omega} = x,$$

$$\frac{\kappa}{\omega} = \alpha,$$

and

$$\tfrac{3}{4}\lambda = \beta.$$

In this way (8) becomes

$$\left.\begin{array}{c} [1 - x^2 - \beta(a^2 + b^2)]a - 2\alpha xb = E, \\ [1 - x^2 - \beta(a^2 + b^2)]b + 2\alpha xa = 0. \end{array}\right\} \quad (9)$$

Let us further write

$$y = a^2 + b^2,$$

where y is the square of the amplitude A for stationary conditions. In this way (9) becomes

$$(1 - x^2 - \beta y)^2 y + 4\alpha^2 x^2 y = E^2, \quad . \quad . \quad . \quad (10)$$

a cubic equation in y, the real roots of which give us the values of the possible stationary amplitudes.

But the possible amplitudes are not necessarily stable. We must therefore determine the criteria of stability for each solution. In determining such criteria we may follow the ordinary methods of dynamics and, in considering the effect of a small change of amplitude due to some disturbing cause, investigate whether the amplitude tends to return to or depart further from its initial stationary value. Thus, let us suppose that the oscillatory system is disturbed so that a becomes $a + \Delta a$ and b becomes $b + \Delta b$, where Δa and Δb are small. On making these substitutions in (7) and neglecting squares of small quantities, we have

$$\left.\begin{array}{c} [2\alpha D + (1 - x^2) - 3\beta a^2 - \beta b^2]\Delta a \\ + [-2xD - 2\alpha x - 2\beta ab]\Delta b = 0, \\ [2xD + 2\alpha x - 2\beta ab]\Delta a \\ + [2\alpha D + (1 - x^2) - \beta a^2 - 3\beta b^2]\Delta b = 0, \end{array}\right\} \quad (11)$$

where D has been written for $\dfrac{1}{\omega}\dfrac{d}{dt}$. Assuming $\Delta a = F e^{mt}$

and $\Delta b = G e^{mt}$, we obtain a quadratic equation for m, namely,

$$A m^2 + B m + C = 0, \quad . \quad . \quad . \quad . \quad (12)$$

where

$$A = 4\alpha^2 + 4x^2,$$

$$B = 4\alpha(1 + x^2 - 2\beta y),$$

and

$$C = (1 - x^2)^2 + 4\alpha^2 x^2 - 4\beta y(1 - x^2) + 3\beta^2 y^2.$$

Now, for the amplitudes a and b to be stable, the roots of the equation for m must have a negative real part. Thus for stability we must have

$$\left.\begin{array}{l} A > 0, \\ B > 0, \\ C > 0. \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

It is obvious that the first of these conditions is always satisfied, and it will be shown later that the second is always satisfied for the experimental conditions we are considering. But the third condition is sometimes not fulfilled for normal experimental conditions, indicating cases of possible but unstable amplitudes.

In elucidating the various facts concerning the possible amplitudes and their stability, we shall find it convenient to think in terms of the ordinary resonance curve as exemplified in fig. 2. The variables x and y have been so chosen that the relation (10) plotted in the ordinary way gives us theoretical curves of this type. Before plotting such curves, however, we may consider the value of the tangent $\dfrac{dy}{dx}$ at various points. On differentiating (10) with respect to x, we have

$$\frac{dy}{dx} = \frac{4xy(1 - x^2 - 2\alpha^2 - \beta y)}{(1 - x^2)^2 + 4\alpha^2 x^2 - 4\beta y(1 - x^2) + 3\beta^2 y^2},$$

or

$$\frac{dy}{dx} = \frac{D}{C},$$

where

$$D = 4xy(1 - x^2 - 2\alpha^2 - \beta y),$$

and, as previously,

$$C = (1 - x^2)^2 + 4\alpha^2 x^2 - 4\beta y(1 - x^2) + 3\beta^2 y^2.$$

We may further note that $C = 3C_1C_2$, where

$$C_1 = \tfrac{2}{3}(1-x^2) + \tfrac{1}{3}(1-x^2)\sqrt{1 - \frac{12\alpha^2 x^2}{(1-x^2)^2}} - \beta y,$$

and

$$C_2 = \tfrac{2}{3}(1-x^2) - \tfrac{1}{3}(1-x^2)\sqrt{1 - \frac{12\alpha^2 x^2}{(1-x^2)^2}} - \beta y.$$

Thus for the series of resonance curves mentioned above, the following general summary may be made :—

  (a) The tangents of the resonance curves are horizontal for points on the curve $D=0$.

  (b) The tangents of the curves are vertical at points on the two curves $C_1=0$ and $C_2=0$.

  (c) An amplitude value is stable only when $C>0$ and $B>0$.

These points may further be illustrated by fig. 4, in which the curves $D=0$, $C_1=0$, $C_2=0$, and $B=0$ are drawn for the resonance region, where x is approximately equal to unity.

The values of the ordinates for the curve $B=0$ are much larger than the corresponding ordinates of the other curves. This is indicated by the break in the axis of $\sqrt{\beta y}$. With the aid of this diagram we may examine the stability of the various solutions. In doing this it is convenient to divide the diagram into regions, as numbered in the figure, and tabulate the data as follows :—

Region.	D.	C_1.	C_2.	C.	B.	Nature of Oscillation.	$\frac{dy}{dx}$.
1	+	+	+	+	+	Stable.	+
2	+	+	−	−	+	Unstable.	−
3	+	−	−	+	+	Stable.	+
4	−	−	−	+	+	Stable.	−
5	−	−	−	+	−	Unstable.	−

The regions of instability indicated by this table have been

shown shaded in fig. 4.   The unstable region above the curve
$B=0$ is never reached in actual practice.

Fig. 4.
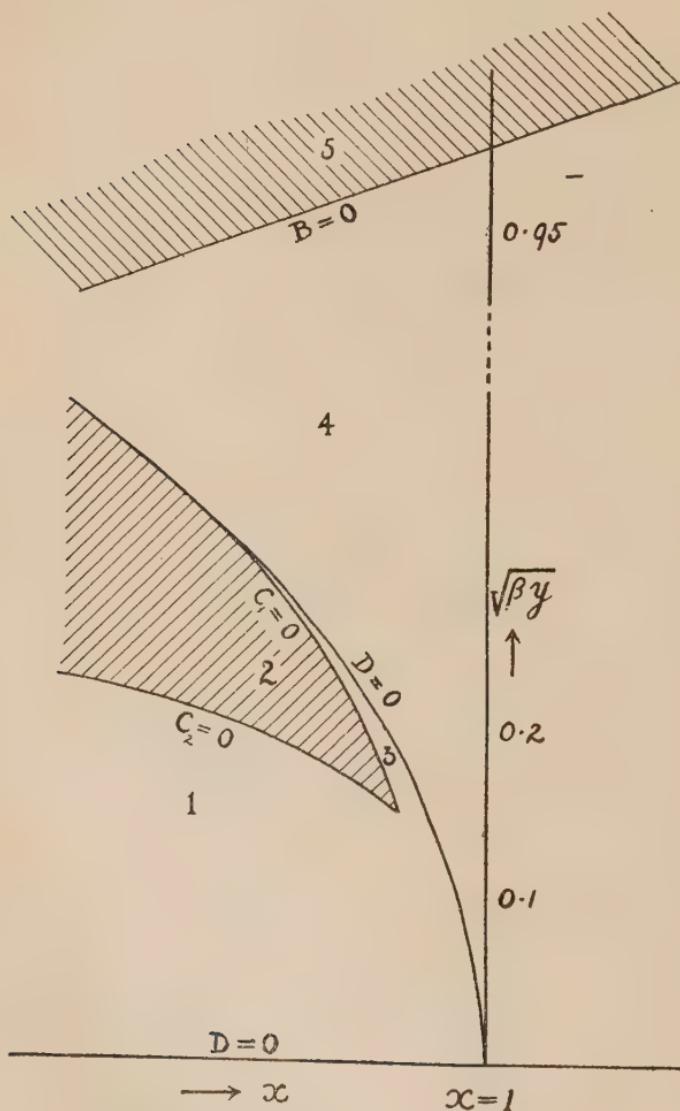
A complete series of theoretical resonance curves are shown
in fig. 5.   These were drawn using equation (10).   The
points of horizontal tangent $(D=0)$ and the points of
vertical tangent $(C=0)$ are also shown.   In accordance with
the results of the table the amplitudes indicated by the dotted
lines are unstable.

Fig. 5.
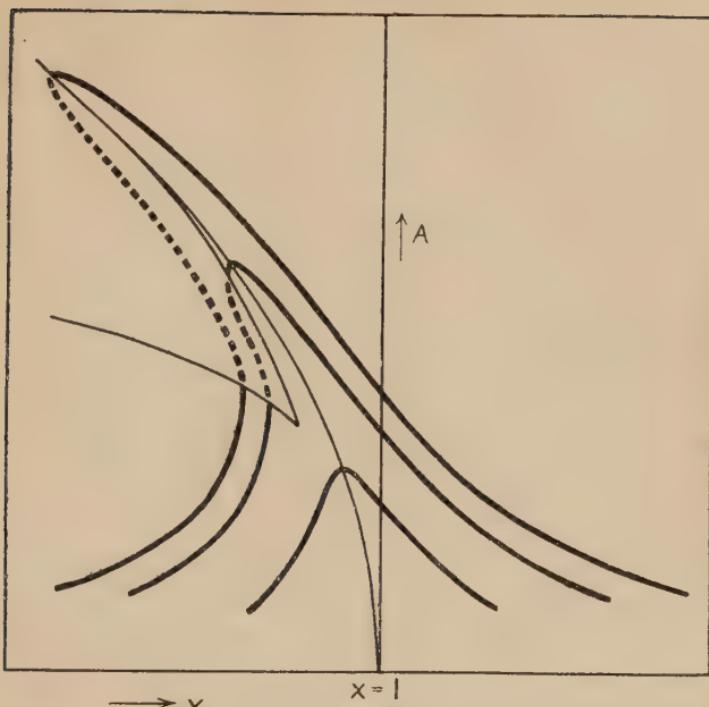
Showing theoretical resonance-curves.

It wiil be seen that the theoretical curves of this figure are of a type similar to the experimental curves shown in fig. 2.

Cambridge, August 1923.

(*Note.*—While this paper was in course of communication, a paper by F. Waibel appeared in the *Annalen der Physik*, lxxii. p. 3, no. 19 (1923), in which a case of oscillation-hysteresis in a vibration-galvanometer is recorded, but no theory of the behaviour is given.)

LVI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 480.]

January 9th, 1924.—Prof. A. C. Seward, Sc.D., F.R.S., President, in the Chair

THE following communications were read :—

1. 'The Geological Structure of the Clevedon–Portishead Area (Somerset).' By Prof. Sidney Hugh Reynolds, M.A., Sc.D., F.G.S., and Edward Greenly, D.Sc., F.G.S.

The area described is, in the main, a prominent ridge some 4 miles long, forming the extreme north-western portion of Somerset

and extending between the small towns of Clevedon and Portishead. It is one of a number of similar ridges in Northern Somerset composed of Carboniferous Limestone alone, or of Carboniferous Limestone and Old Red Sandstone, but differs from all the others in that it trends north-east and south-west, instead of east and west.

The main part of this ridge is of very simple structure, consisting of Old Red Sandstone overlain by Carboniferous Limestone (K, Z, and C beds) dipping south-eastwards at an angle which averages about 35° to 40°. These rocks form the north-western limb of a synclinal fold, the south-eastern limb of which is seen only in a series of isolated exposures at Clevedon, at Weston Big Wood, and at Portishead. At Weston Big Wood, where the rocks of the south-eastern limb are vertical or slightly overfolded, nothing below Z_2 is seen; but at Portishead a south-westerly pitch in the axis of the fold brings the lowest Carboniferous and Old Red Sandstone to the surface, the rocks being (as at Weston Big Wood) usually vertical or slightly overfolded. At the Clevedon end the infold pitches north-eastwards, and beds as high as the Coal Measures are involved.

The folding along the dominant north-east and south-west axis was accompanied by overthrusting from the south-east, which caused *Caninia* Oolite (C_1) to be driven over the Coal Measures and the Z beds over the *Caninia* Oolite at Bella Vista, Clevedon; while Dial Hill, Clevedon, consists of an overthrust outlier of steeply inclined C beds resting partly on C beds, but mainly on Z beds, and Fore Hill, Portishead, one of gently dipping Z beds resting upon vertical Old Red Sandstone. At both ends of the area there are further complications, leading in each case to a partial resumption of the east-and-west strike.

At Portishead the transverse disturbance seems to take the form of a northward thrusting of the main body of the ridge over the east-and-west striking rocks of the Eastwood Ridge.

At the Clevedon end the transverse disturbance has also the form of a northward overthrust, the members of the north-east and south-west series being again driven over the east-and-west series; but here one of the major thrust-planes of the north-east and south-west series appears to be involved in the disturbance, and doubled back on itself at the Hill Road Crag, Clevedon.

2. 'The Avonian of the Tytherington–Tortworth–Wickwar Ridge (Gloucestershire).' By Frederick Stretton Wallis, Ph.D., F.G.S.

The author describes and maps, in terms of Vaughan's system of zonal nomenclature, the northern portion of the horseshoe-shaped ridge of Avonian rocks which partly surrounds the synclinal basin of the Bristol Coalfield. The chief points of interest may be summarized as follows :—

    (1) The recognition of all zones, with the exception of the *Dibunophyllum* Zone.

(2) The great expansion and fossiliferous character of the 'Sub-Oolite' bed as compared wth that exhibited in the type-section of the Avon.

(3) The early incoming of 'Millstone Grit' conditions at the top of S_2 adds a further link to the accumulated evidence regarding the entrance of this sandy phase at progressively lower horizons north of Bristol.

3. 'The Avonian of the Western Mendips, from the Cheddar-Valley Railway to the Sea, west of Bream Down.' By Miss Agnes Elizabeth Bamber, M.Sc.

Comparison is made between the Avonian of the Western Mendips, and (*a*) the Avon section and (*b*) the Burrington Combe section. The outcrops of the Carboniferous Limestone zones have been mapped, the zonal notation of the late Dr. Vaughan being utilized. Levels from K_2 to S_1 are exposed in the area. The lithological and palæontological characters are described.

The usefulness of the application of Vaughan's zonal notation to Carboniferous Limestone outside the Bristol area has been again proved. The conclusions arrived at by Principal T. F. Sibly, and stated in his Mendip paper, have been confirmed. With the exception of the C_2 to S_1 beds, the lithological sequence in the Western Mendips is essentially similar to that of the Avon section. *Modiola*-phase conditions in S_1 extended to the Western Mendips, but were not completely established there. The divergence from C_2–S_1 conditions of the Avon section is slightly less in the Western Mendips than at Burrington. K_2, β, and Z_1, hitherto unrecorded from the area, are exposed. *Conocardium* sp. and *Spiriferina* (probably an early form of *insculpta*) have been recorded from low in γ, and *Cyathophyllum* θ from the lowest beds of C_1.

January 23rd.—Prof. A. C. Seward, Sc.D., F.R.S.,
President, in the Chair.

The following communication was read :—

'On a Recently Discovered Breccia-Bed underlying Nechells (Birmingham), and its Relations to the Red Rocks of the District.' By Prof. William S. Boulton, D.Sc., F.G.S.

A recent boring for water at Nechells Gasworks (Birmingham) has revealed an unexpected succession of rocks, which appear to have an important bearing on the problem of the 'Permian' of the Midlands and its relation to the Carboniferous and Trias.

The cores from the boring are described in detail, and it is shown that here the Keuper Sandstone (272 feet thick) rests unconformably upon a coarse breccia (Nechells Breccia) 350 feet thick, which in turn rests unconformably on Hamstead Beds (Calcareous Conglomerate Group).

The Breccia consists of angular fragments and lumps, up to a foot or more across, derived for the greater part from Cambrian quartzite and sandy limestone with some decomposed volcanic rocks ; and in the lower portion, the fragments are calcareous

sandstone of the type of the underlying Hamstead Beds. Thin beds of marl and sandstone are interbedded with the Breccia.

Fossils, belonging to the horizon just below the *Olenellus* Limestone at Comley (Shropshire) and to the horizon of the *Hyolithus* Beds at the top of the Hartshill Quartzite of Nuneaton, have been collected from lumps of the sandy limestone in the Breccia.

The extension of the Nechells Breccia underneath other parts of the Birmingham area is discussed, and evidence is adduced to show that the Bunter Beds on the west of Nechells thin out against the rising bank of Breccia ; also that the Nechells Breccia was derived from an old land-surface very near Birmingham, probably on the south-east.

The relations of the Nechells Breccia to those of Hopwas and Clent are then dealt with, and evidence put forward for an unconformity at the base of the Clent Breccia. The foregoing are grouped with the Leicestershire Breccias described by Dr. H. T. Brown in 1889, with the Polesworth Breccia of North Warwickshire, and with that found in the Burcot Boring near Bromsgrove.

Thus breccias occur at intervals in a belt 40 miles long from north-east to south-west, all, so far as known, unconformable to the beds below them, and to the Trias above. Generally speaking, the material of these breccias was derived from rocks which increase in age from north to south.

The correlation of the marls with fine breccias in the Warley area, 3 to 4 miles west of Birmingham (which are apparently conformable to the Calcareous Conglomerate Group below, and were regarded by Mr. Wickham King in 1899 as the equivalent of the Clent Breccia on the south), is left in doubt until such further evidence is discovered as will show whether they are older than the Clent Breccias, and not separated from the underlying beds by a time-break ; or whether they represent deposits in water-basins contemporaneous with the accumulation of the Clent Breccias.

The Breccia Group (Manor House and Tower Hill sub-groups of Mr. W. H. Hardaker), in the Hamstead Quarry Series, described by him in 1912, is shown not to exist as such, but to be part of the Calcareous Conglomerate Group.

Instances are given of Midland breccias of Triassic age, and the difficulty of discriminating in some cases between original Permian breccias and basement Triassic deposits made up of their derived material is considered.

The classification of the pre-Triassic Red Rocks of the Midlands recently adopted by the Geological Survey is discussed, and the following grouping is suggested :—

(3) Clent Beds (Breccias of Clent, Northfield, Nechells, Hopwas, etc.).
(Unconformity)

(2) Corley Beds (the Calcareous Conglomerate Group, with, in the meantime, the Warley and Kingswinford Marls and intercalated fine breccias of South Staffordshire, and the Tile Hill Marls and Sandstones of Warwickshire).

(1) Keele Beds.

The age of the Corley Beds, which follow conformably upon the Keele, is still uncertain, and may eventually prove to be Permian ; but the author agrees with the Geological Survey that (for the present) it is convenient to group them with the Carboniferous. The evidence now brought forward points unmistakably to the Permian age of the Clent Beds, in which the Nechells Breccia is included.

February 6th.—Prof. A. C. Seward, Sc.D., F.R.S.,
President, in the Chair.

The following communication was read :—

'The Upper Towy Drainage-System.' By Prof. Owen Thomas Jones, M.A., D.Sc., F.G.S.

The paper gives an account of the physical and main geological features of the upper part of the Towy drainage-system. The floors of the Towy valley and of its principal tributaries (the Camddwr and Pysgotwr) were levelled, in order to obtain data for constructing their longitudinal profiles. A few levels were also determined in the upper valley of the Cothi, which formerly entered the Towy valley many miles above its present mouth.

The Towy valley, for about 8 miles from the source, is fairly wide, and the opposing spurs, which usually are gently convex, are set well apart ; the longitudinal profile is concave, and the lower ends of the tributary valleys are graded with the main valley. The features are those of a fully mature drainage-system. Above Fanog (8½ miles) the floor of the valley is trenched by a narrow ravine, which develops into a deep glen gradually widening downstream. Between Rhandirmwyn (15 miles) and Llandovery (22 miles) the valley presents once more a mature appearance, which it retains as far as its mouth (56 miles) below Carmarthen. The whole longitudinal profile thus consists of two concave portions, in each of which the gradient diminishes progressively downstream, separated by a short stretch with high and irregular gradient.

The upper part of the valley is attributed to a former period of base-levelling. This was followed by a rejuvenation of the drainage-system due to an uplift of the area. The present valley between Rhandirmwyn and the mouth was eroded in consequence of that rejuvenation, and is base-levelled or graded in relation to the existing sea-level. The upper or Fanog base-level, as it is termed, to which the upper part of the valley conforms, now stands much above the present sea-level. A formula was sought and found to which the profile above Fanog conforms ; also the height of the Fanog base-level at the present mouth of the Towy was determined by calculation from the formula, and by comparison with the profile and gradient of the valley below Llandovery. These determinations show a difference of approximately 400 feet between the former and the existing base-levels.

The tributary valleys afford confirmation of the results obtained in the main valley. About half a mile above Nant Stalwyn

(5 miles) there is a well-marked drop or step in the rock-floor of the Towy valley. Below this step the tributary valleys hang above the main valley-floor, the discordance increasing downstream. The association of a rock-step with hanging valleys below is often regarded as evidence of Glacial erosion with overdeepening of the main valley: but, in this locality, there is conclusive evidence that the hanging tributaries are pre-Glacial. The most probable explanation of these features is that they are due to a still earlier uplift of the region, followed by rejuvenation of the valley up to the rock-step. This suggestion is borne out by the features of the tributary valleys for many miles downstream.

The part of the valley above the rock-step was, therefore, eroded in relation to a base-level older than the Fanog base-level. This, which is termed the Nant Stalwyn base-level, is estimated to stand at present nearly 600 feet above the level of the sea.

The investigation has also thrown light on past changes in the drainage-system, and may ultimately help to solve the problem of the age and origin of the great plateau of Central Wales.

LVII. *Intelligence and Miscellaneous Articles.*

INCREASE OF INERTIA OF BODIES VIBRATING IN A LIQUID.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the December number of the Philosophical Magazine there appears a note by N. C. Krishnaiyar, M.A., on the "Increase of Inertia of Bodies Vibrating in a Liquid."

His paper deals only with experiments on the increase of inertia of a sphere; and I think it may be of interest to mention some approximate values that I have been able to obtain experimentally for the increase of inertia of a marine propeller vibrating under water. The experiments have been carried out in two ways:—
(1) By obtaining a curve of the amplitude of a forced vibration, and so determining the natural frequency of the system of engine, shafting, and propeller: the inertia of all other parts being known, it is easy to calculate the propeller inertia. (2) If a forced vibration is caused by the engine, the propeller inertia may be determined from the position of the node of forced vibration.

Experiments on the above lines have shown that the value of the inertia factor varies, with different shapes of propeller blade, from 2 to about 4. A knowledge of the value of the inertia factor is, of course, necessary before a calculation can be made of the natural frequeucy of torsional vibration of a marine-engine shafting ; and with this object in view, I hope shortly to be able to carry out further experiments on the influence of the shape of a body on its inertia factor when vibrating in water.

9 Bentinck Crescent,	Yours faithfully,
	Newcastle-on-Tyne,
	Dec. 19, 1923.	JAMES CALDERWOOD.